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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on page 3 of the Journal cover. New tables will be announced from time to time as they become available.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1435

Part of Journal of Research of the National Bureau of Standards, Volume 27, December 1941

RELATION OF ELECTROMOTIVE FORCE TO THE CONCENTRATION OF DEUTERIUM OXIDE IN SATURATED STANDARD CELLS

By Langhorne H. Brickwedde and George W. Vinal

ABSTRACT

Characteristics of saturated cadmium cells, containing small percentages of deuterium oxide (D_2O), were described in an earlier paper. The work has since been extended to include various concentrations up to 98 mole percent of D_2O. For each group of the cells, crystals of cadmium sulfate were prepared in equilibrium with the isotopic composition of the respective saturated solutions. At 98 mole percent of D_2O the electromotive force is 388 microvolts less than that of the control cells containing normal water. The relation between the electromotive force of the cells and the D_2O content of the water is linear from 0 to 50 percent. Above 50 percent the electromotive force is decreased slightly more. The changes in electromotive force with temperature, hysteresis effects, and internal resistance of the cells were measured. Observations on cells made 4 years ago, as well as those made more recently, justify the conclusion that cells containing D_2O are as reproducible and constant as the more usual type made with normal water. The difference between the partial molal free energy of $CdSO_4$ in H_2O and D_2O solutions is calculated.

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I. INTRODUCTION

The effect of small percentages of deuterium oxide (D_2O) on the properties of saturated standard cells was reported by the present authors in a previous paper [1].[1] This work has now been extended to include the preparation of cells containing D_2O up to 98 mole percent. Predictions based on the former work have been substantially confirmed by the behavior of cells containing higher percentages.

[1] Figures in brackets indicate the literature references at the end of this paper.

Practical reasons for continuing the work are based on the desirability of obtaining modified forms of saturated standard cells which are equal, if not superior, to those now in use as standards of electromotive force. The earlier cells and those described in this paper are as reproducible and constant as control cells made with ordinary water, but observations extending over a much longer period of time are needed before conclusions can be drawn about their serviceability as primary standards of electromotive force.

There is considerable theoretical interest also in the effect of D_2O on the electromotive force of a system which can be measured to a high degree of precision.

In the earlier work 12 saturated cadmium cells containing several different concentrations from 0 to 5 mole percent of D_2O were constructed. The new group comprises 17 cells in all, and it is divided into 5 subgroups of 3 or more cells each, containing 0, 6, 49, 81, and 98 mole percent of D_2O, respectively.

Several problems developed in the course of the work. Those relating to solubility of the salt and properties of the solutions will be described in a subsequent paper. Unforeseen conditions of metastability of cadmium sulfate were found, and the transition temperature from $CdSO_4.8/3\ H_2O$ to $CdSO_4.\ H_2O$ was fixed by both electromotive force and solubility measurements at about 43° C, which is 30° lower than previously reported. The results on cells in a metastable condition have been reported in another paper [2].

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF MATERIALS

Some modifications of the usual procedure in making standard cells were required to avoid dilution of the D_2O solutions by ordinary water and to avoid evaporation. Since each solution was to be saturated with anhydrous cadmium sulfate, it was necessary first to determine the comparative solubility of the salt in ordinary water and in the respective solutions of D_2O. This was done at several temperatures.

Crystals of cadmium sulfate carrying the usual water of crystallization and other samples in equilibrium with the D_2O content of the respective solutions were also needed to make cells of the saturated type. As a preliminary, a purified sample of cadmium sulfate was dehydrated in a muffle furnace at a temperature of 650° to 700° C. A trace of SO_3 in the atmosphere was maintained throughout the process by bubbling air slowly through a tower containing fuming sulfuric acid and then through the furnace. The completeness of dehydration was tested by reheating a weighed sample. This dehydrated salt was used for saturating solutions which were employed in the cells and from which crystals were grown under controlled conditions.

To form crystals in equilibrium with the respective solutions, a closed system consisting of two flasks connected by a glass tube was employed. The system having been evacuated, the flask containing the saturated solution was gently warmed to a few degrees above room temperature by its proximity to a small electric-light bulb, while the other flask was immersed in an ice bath. Water was slowly evaporated from the first flask and condensed in the second. The

rate of evaporation was regulated to grow crystals of convenient size for use in the cells. By this means the necessary materials were provided without waste of the D_2O. Unlike the earlier cells made with small percentages of D_2O, no question of the exchange of the water of crystallization is involved.

Except for differences in the isotopic composition of the water, all materials used in constructing the cells were identical. Methods of purifying these materials, other than the water, have been described in an earlier publication [3].

Each sample of water was purified by distillation. Samples containing appreciable amounts of D_2O were distilled slowly in a closed system under reduced pressure. Normal water was twice distilled, as we have ordinarily done in the past, the second distillation being made from a phosphoric acid solution in a special still with scrubbers and air purifiers. The conductivity of this water was 0.1×10^{-6} ohm^{-1} cm^{-1} at the time of distillation.

2. CONSTRUCTION OF THE CELLS

The details of constructing the cells were essentially those which the authors have followed in previous work. Mercurous sulfate sufficient for all cells was first washed in the customary manner. A portion of it was then made into a paste with the saturated solution of cadmium sulfate and crystals. This paste was employed in the first subgroup of cells containing normal water. The succeeding subgroups of cells containing D_2O were then made in the order of increasing mole percentages. For each of these the mercurous sulfate was washed with two portions of the corresponding solution. The paste for each subgroup was made by mixing the mercurous sulfate with the saturated solution and the crystals of cadium sulfate which were in equilibrium with it. Each subgroup therefore contained paste made with cadmium sulfate solution and crystals of the same D_2O content as that used in filling the cells. Throughout the work care was taken to avoid undue exposure of the D_2O solutions. After all cells were completed they were hermetically sealed.

A new and improved method of introducing the amalgam into the cells was employed. This has not been described before. The hot amalgam was prepared by warming the required amounts of cadmium and mercury together in an electrically heated closed separatory funnel. The stem of the funnel was also electrically heated, and the amalgam flowed freely from the reservoir above when the stopcock was opened. This stopcock was free from lubricants of any kind. The amalgam introduced into the cells in this way was always bright and free from traces of scum which are sometimes observed under other conditions. This method of introducing the amalgam was found to be superior to the ordinary methods of ladling or the use of pipettes.

The determination of acidity of the cells, approximating 0.04 *N* acid, presented some experimental difficulties. The amount of sulfuric acid which was added was determined by weight, and in the case of cells containing normal water, the acidity was checked by direct titration. The acidities of the respective groups varied from 0.035 to 0.042 *N* acid.

3. DETERMINATION OF D_2O CONTENT

Although in water containing D_2O and H_2O there is also HDO present, throughout this paper the total amount of deuterium present has been referred to as D_2O and its concentration expressed as the mole percent of D_2O of the total water present.

In order to establish a relation between the electromotive force and the D_2O content of the solution in the cell, it was necessary to determine the mole percentage of D_2O in the water of the saturated solution. The D_2O contents were found as follows: Densities of the distillates removed in forming $CdSO_4.8/3$ (H_2O, D_2O) crystals in each saturated solution were determined with a 0.4-ml picnometer. The D_2O content of each distillate was then computed from the observed densities and the relation of D_2O to density as given by Swift [4]. This does not, however, correspond exactly to the D_2O content of the water of the saturated solutions in the cell. To find the D_2O content of the saturated cadmium sulfate solution, we have assumed that the ratio of D_2O/H_2O in the vapor over these solutions is the same as the ratio of D_2O/H_2O in the vapor over water in which no salt is dissolved. This assumption seemed justified in order to avoid sacrificing the completed cells for a direct analysis and in view of the fact that the D_2O content need be known only to 0.3 mole percent, which corresponds to a difference of 1 microvolt in the electromotive force.

In making this calculation, we have followed the procedure outlined by Smith and Wojciechowski [5] for calculating the D_2O concentration in the liquid phase from the measured D_2O concentration in the distillate. These values are given in table 1.

TABLE 1.—*Deuterium oxide concentration in the cells*

Cells	Picnometer measurement of distillate [a]	Mole percent of D_2O in distillate	Calculated mole percent of D_2O in residue
991 to 995	1.00000	0.02	0.02
996 to 998	1.00653	6.1	6.5
999 to 1001	1.05114	47.4	49.0
1002 to 1004	1.08572	79.6	80.6
1005 to 1007	1.10575	98.2	98.3

[a] In Swift's notation this is $d^{25}_{D_2O}/d^{25}_{T=\infty,\ H_2O}$

4. ELECTRICAL MEASUREMENTS

Electromotive forces of the cells were measured in terms of the group of cells which serves as the United States primary standard for the International volt. Each cell was connected in opposition to the primary reference cell, and the difference in electromotive force between the cells was measured with a special potentiometer designed by Brooks [6] for standard-cell comparisons. Instrumental errors were probably less than 0.3 microvolt.

Both the experimental cells and the primary reference cell were kept at constant temperature in oil baths controlled to $\pm 0.006°$ C or less. The primary standard is maintained at 28° C, and the experimental cells were measured at 17°, 20°, and 28° C.

In order to compare cells of the various subgroups, small adjustments in the values of electromotive force have been made to compensate for differences in acidity. The acidities varied from 0.035 to 0.042 *N* acid, but the electromotive forces of the new cells are reported on the uniform basis of 0.040 *N* acid. The maximum correction in any case to bring the values to this common basis did not exceed 3 microvolts.

III. EXPERIMENTAL RESULTS

1. ELECTROMOTIVE FORCE OF THE CELLS

The electromotive-force measurements at 20° and 28° C are given in table 2. The value for each cell is the mean of five measurements at each temperature taken over a period of at least 5 days. The consistency of electromotive-force measurements is indicated by the small mean deviations of a single observation, as shown in columns 5 and 6 of the table. As in the earlier paper [1], the results are consistent in showing the effect of D_2O in decreasing the electromotive force approximately in proportion to the amount present.

TABLE 2.— *Electromotive forces of individual cells*

Cells	D_2O content	Electromotive force (average) (adjusted to 0.040 *N* acid)		Mean deviation of single observation	
		at 20.00°C	at 28.00°C	20°C	28°C
	Mole percent	*Int. volts*	*Int. volts*	*μv*	*μv*
991	0.02	1.018264$_7$	1.017890$_9$	±0.5	±0.7
992	.02	66$_3$	93$_0$	.2	.6
993	.02	66$_6$	93$_2$	.4	.5
994	.02	67$_9$	93$_2$	.4	.5
995	.02	66$_2$	91$_8$	.1	.3
Mean	0.02	1.018266$_9$	1.017892$_4$		
996	6.5	1.018240$_7$	1.017868$_2$	0.5	0.4
997	6.5	45$_1$	70$_7$	.3	.1
998	6.5	43$_2$	69$_3$	.4	.3
Mean	6.5	1.018243$_0$	1.017869$_4$		
999	49.0	1.018091$_8$	1.017719$_2$	0.3	0.5
1000	49.0	88$_4$	18$_8$	.8	.4
1001	49.0	91$_4$	19$_8$	.4	.3
Mean	49.0	1.018090$_3$	1.017719$_7$		
1002	80.6	1.017961$_9$	1.017590$_1$	0.6	0.3
1003	80.6	63$_9$	92$_8$	.2	.3
1004	80.6	64$_2$	92$_1$	.2	.2
Mean	80.6	1.017963$_9$	1.017591$_4$		
1005	98.3	1.017877$_9$	1.017505$_9$	0.3	0.6
1006	98.3	78$_9$	05$_3$	.5	.5
1007	98.3	78$_4$	05$_4$	.4	.3
Mean	98.3	1.017878$_9$	1.017505$_4$		

2. RELATION OF ELECTROMOTIVE FORCE TO D_2O CONTENT

The mean electromotive force of each subgroup at 20° C is plotted in figure 1 with respect to the mole percent of D_2O in the water of the cells. The curve is nearly linear. On the average the decrease

in electromotive force is about 4 microvolts per mole percent of D_2O, but this varies from 3.6 for the lower concentrations to 5.3 at the highest concentration. The detailed results are given in table 3. For concentrations less than 50 mole percent of D_2O the relationship

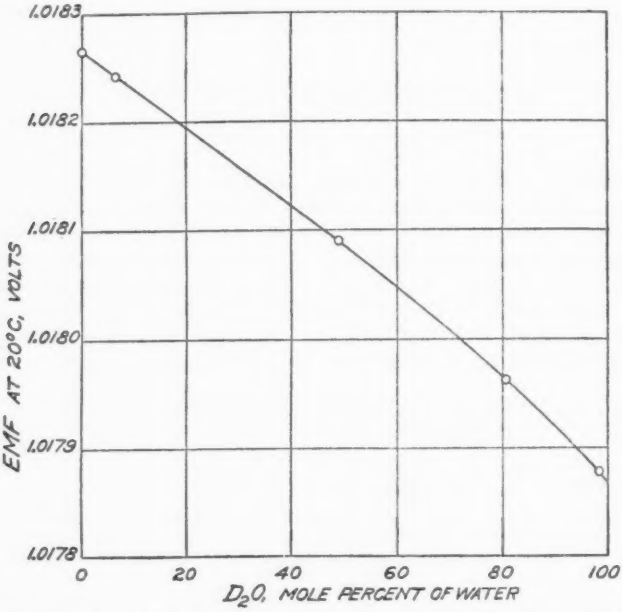

FIGURE 1.—*Relation of electromotive force to the concentration of deuterium oxide*

is linear. Above 50 percent the effect of the D_2O becomes proportionately greater. In table 3 the values for ΔE per mole percent are given as the tangents to the curve measured at the respective points.

TABLE 3.—*Changes in electromotive force with* D_2O *content*

Cells	D_2O content	ΔE = difference from control cells	ΔE per mole percent (tangent to curve)
	Mole percent	*μv*	*μv*
991 to 995 *	0.02		
996 to 998	6.5	23.4	3.6
999 to 1001	49.0	175.8	3.6
1002 to 1004	80.6	303.3	4.4
1005 to 1007	98.3	388.3	5.3

* Control cells, containing normal water.

Table 4 gives the electromotive forces for the acid cells used in these experiments, at even percentages of D_2O. These values were read from the curve in figure 1. Estimated values for the Weston normal (neutral) cell are also included for corresponding percentages of D_2O.

TABLE 4.—*Effect of D_2O on the electromotive force of the Weston normal cell*

Percentage of D_2O in the water	Observed decrease in electromotive force	Electromotive force of cell at 20°C (0.04 *N* acid)	Estimated electromotive force of Weston normal cell
	μv	*Int. volts*	*Int. volts*
0		1.018267	• 1.018300
10	36	8231	8264
20	72	8195	8228
30	108	8159	8192
40	144	8123	8156
50	180	8087	8120
60	219	8048	8081
70	259	8008	8041
80	302	7965	7998
90	348	7919	7952
100 (extrapolated)	399	7868	7901

• The Weston normal cell has an electromotive force at 20°C of 1.018300 Int. volts by definition.

3. TEMPERATURE COEFFICIENT AND HYSTERESIS

Measurements of electromotive force were made at 17°, 20°, and 28° C for the purpose of determining how nearly the temperature coefficient of these cells agrees with the generally accepted value based on the International temperature formula [7]. Observed differences in electromotive force at these temperatures are given in table 5. The differences in electromotive force are based on values observed after ample time had been allowed for the cells to reach equilibrium at each temperature.

It is evident from these data that the temperature coefficient is practically independent of the D_2O content. Observed differences are in better agreement with the formula of Vigoureux and Watts [8] than with the International formula.

The authors have found by experience with other groups of acid cells that the observed difference, $E_{20}-E_{28}$, is substantially in agreement with the present experimental results, that is, less than the value which would be calculated from the International formula.

TABLE 5.—*Change in electromotive force with temperature, and hysteresis measurements*

Cells	D_2O content	Values of $\Delta E/\Delta t$		Hysteresis effect •	
		17° to 20° C	20° to 28° C	20° to 28° C	28° to 20° C
	Mole percent	*μv per 3° C*	*μv per 8° C*	*μv*	*μv*
991 to 995	0.02	110.8	373.9	−2	−25
996 to 998	6.5	110.9	373.6	−1	−35
999 to 1001	49.0	109.7	371.3	−3	−17
1002 to 1004	80.6	108.3	371.6	−2	−5
1005 to 1007	98.3	109.3	372.6	−1	−6
By International formula		113.0	380.8		
By formula of Vigoureux and Watts		109.8	370.1		

• Electromotive forces observed 2 to 3 hours after temperature change minus equilibrium electromotive force at new temperature.

When changing the temperature of the cells from 20° to 28° C and back to 20° C, they were removed from one oil bath and plunged into another at a different temperature. These sudden temperature changes would be reflected in abnormal electromotive forces if the cells were subject to hysteresis. Two to three hours were allowed for

thermal equilibrium to be established, and the electromotive forces were then read and recorded for comparison with equilibrium values obtained later. The differences, which may be taken as a measure of the hysteresis effect, are given in table 5. It is apparent that hysteresis of all the cells was less when an increase in temperature occurred than when the temperature was decreased by the same amount. This is in line with common experience. The most noteworthy feature of the measurements is to show that hysteresis is less in the cells having the higher concentrations of D_2O, but some irregularities may have been caused by variations of the size of crystals in cells of the various subgroups.

4. INTERNAL RESISTANCE

The internal resistance of standard cells is a useful criterion of their condition. Generally the internal resistance increases somewhat with age. If this occurs in unsaturated cells, the increase in resistance is usually an indication that a gas bubble has formed between the surface of the amalgam and the diaphragm. In saturated cells, the increase in resistance may be the result of (1) coalescing of the crystals of cadmium sulfate, (2) the formation of small crystals which tend to fill the interstices between larger crystals, and (3) the formation of gas. Cells of the usual type illustrated in a paper by the present authors [9] have an initial resistance of 500 to 700 ohms at 28° C. The exact value of resistance in this range is not a matter of importance, and it varies considerably with small differences in dimensions and other details of construction. If the resistance increases to 1,200 ohms or more, the cells are likely to be unreliable.

TABLE 6.—*Resistance of cells at 20° and 28° C*

Cells	D_2O content	Resistance at—		Ratio R_{20}/R_{28}
		20.00° C	28.00° C	
	Mole percent	*Ohms*	*Ohms*	
991	0.02	962	706	1.36
992	.02	701	567	1.24
993	.02	656	524	1.25
994	.02	827	649	1.27
995	.02	754	610	1.24
Mean	0.02	780	611	1.27
996	6.5	905	731	1.24
997	6.5	707	554	1.28
998	6.5	707	563	1.26
Mean	6.5	773	616	1.26
999	49.0	732	589	1.24
1000	49.0	1,041	753	1.38
1001	49.0	754	597	1.26
Mean	49.0	842	648	1.29
1002	80.6	881	690	1.28
1003	80.6	823	642	1.28
1004	80.6	971	720	1.35
Mean	80.6	892	682	1.30
1005	98.3	1,053	788	1.34
1006	98.3	834	667	1.25
1007	98.3	779	608	1.28
Mean	98.3	889	688	1.29

Interest in the internal resistances of the cells containing D_2O relates primarily to the effect of substituting deuterium oxide for normal water. Notwithstanding the irregularities of the individual values reported in table 6, the average measurements made at 20° and 28° C are concordant in showing a slight increase in resistance with increasing D_2O content. The average difference between cells containing 98 mole percent D_2O and those with ordinary water is 13 percent. The ratio of resistances for the respective cells at 20° and 28° C is, however, approximately constant irrespective of the D_2O content. This ratio, which averages 1.28 for the present group of cells, agrees substantially with the value 1.24 obtained in the earlier work [1], to which reference should be made for the method of making the measurements.

5. CONSTANCY OF ELECTROMOTIVE FORCE

Periodic measurements of the cells numbered 991 to 1007 have been made during the past 18 months. In addition, similar measurements on the earlier group, Nos. 956 to 967, during a period of 4 years are available. These measurements are summarized in table 7. In general the electromotive forces of cells in the later group, containing the higher percentages of D_2O, have been more constant than in the case of the earlier group, but the same is also true of the respective control experiments, which included cells without the addition of deuterium oxide.

TABLE 7.—*Constancy of electromotive force of cells containing* D_2O

Cells	D_2O content	Electromotive force, 20° C at 6 months	Subsequent changes in electromotive force at—			
			12 months	18 months	30 months	48 months
	Mole percent	v	μv	μ	μv	μv
956 to 958	0.02	[a]1.018273$_0$	+1.$_5$	+3.$_0$	+6.$_0$	+8.$_5$
959 to 961	.76	8270$_5$	+2.$_0$	+3.$_5$	+6.$_5$	+8.$_0$
962 to 964	2.27	8267$_0$	+1.$_5$	+3.$_0$	+6.$_0$	+8.$_0$
965 to 967	4.98	8258$_5$	+1.$_5$	+3.$_5$	+6.$_5$	+9.$_5$
991 to 995	0.02	[b]1.018267$_0$	+1.$_0$	+1.$_5$	----------	----------
996 to 998	6.5	8242$_5$	+0.$_5$	+1.$_0$	----------	----------
999 to 1001	49.0	8090$_5$	+0.$_5$	+1.$_0$	----------	----------
1002 to 1004	80.6	7963$_0$	0.$_0$	0.$_0$	----------	----------
1005 to 1007	98.3	7877$_5$	0.$_0$	0.$_0$	----------	----------

[a] All cells of the group 956 to 967 were 0.03 *N* acid. To correct the electromotive-force values to the same basis as for cells 991 to 1007, subtract 6 microvolts.
[b] The electromotive forces of all cells of the group 991 to 1007 are adjusted to 0.04 *N* acid.

The electromotive force of the earlier cells has increased uniformly during 4 years at a rate of about 2 microvolts per year. It is anticipated that this rate of change will eventually decrease. Several reasons might be assigned for this increase in electromotive force, such as the effect of the glass container in neutralizing part of the acid within the cells. The most significant fact seems to be the uniform behavior of the various subgroups, which have maintained their relative electromotive forces during 4 years.

The later group of cells containing the higher percentages of D_2O have been remarkably constant over a period of 18 months. This was true also of the control cells, Nos. 991 to 995. The electromotive force of these cells is 1.5 microvolts higher now than 1 year previously, but the two groups containing the highest percentages of D_2O, 80

percent in cells 1002 to 1004, and 98 percent in cells 1005 to 1007, have the same respective electromotive forces to within 0.5 microvolt as they had 12 months previously. Whether this result can be attributed wholly to the use of D_2O is not entirely certain. The fact remains, however, that these cells in an early period of their life are as constant as the much larger group of seasoned cells which constitute the Bureau's primary reference standard.

All of the cells made with D_2O have been examined for the formation of gas which sometimes occurs in acid cells, but no significant amount was found in any of them.

In general the results obtained with the later group seem to justify the conclusion given in the earlier paper [1] that cells containing D_2O are fully as reproducible and constant as cells made with normal water.

IV. RELATIVE FREE ENERGY OF $CdSO_4$ IN H_2O AND D_2O SOLUTIONS

Some interesting properties of the cell constituents can be gotten from the thermodynamical comparison of the H_2O and D_2O cells. One can determine the difference in the partial molal free energy of the cadmium sulfate in D_2O saturated with respect to $CdSO_4$. 8/3 D_2O and in an H_2O solution of the same mole fraction of $CdSO_4$. At 20°C a saturated solution contains 0.0602 mole of $CdSO_4$ per mole of D_2O. The electromotive force of the saturated D_2O cell is 1.017868 Int. volts (fig. 1). Since $CdSO_4$ is less soluble in D_2O than in H_2O, an H_2O solution of the same mole fraction is unsaturated at 20°C. From measurements of the relation of electromotive force to $CdSO_4$ composition in cells containing H_2O [10], one calculates the electromotive force of a cell containing 0.0602 mole $CdSO_4$ per mole of H_2O to be 0.00478 volt higher than a cell containing an H_2O saturated solution at 20°C.

For a consideration of the partial molal free energy changes, the reactions for the cells may be written in the condensed form.

$$Cd(\text{amalgam}) + Hg_2SO_4 = CdSO_4(0.0602 \text{ mole per mole } H_2O) + 2Hg \quad (1)$$

$E_{H_2O} = 1.023047$ Int. volts (calculated from emf of saturated H_2O cell).

$$Cd\ (\text{amalgam}) + Hg_2SO_4 = CdSO_4(0.0602 \text{ mole per mole } D_2O) + 2Hg \quad (2)$$

$E_{D_2O} = 1.017868$ Int. volts (observed value)

If eq 2 is subtracted from eq 1, eq 3 is

$$CdSO_4(0.0602 \text{ mole per mole } D_2O) = CdSO_4(0.0602 \text{ mole per mole } H_2O)$$

$$\Delta F_3 = \Delta F_{H_2O} - \Delta F_{D_2O} = [(\overline{F}_{CdSO_4})_{H_2O} - (\overline{F}_{CdSO_4})_{D_2O}]_{\substack{0.0602 \text{ mole } CdSO_4 \\ \text{per mole water}}} \quad (3)$$

$$= -2 \times F(E_{H_2O} - E_{D_2O})$$

$$= -2 \times 96500 \times 0.005179$$

$$= -1{,}000 \pm 20 \text{ Int. joules mole}^{-1}$$

The partial molal free energy of $CdSO_4$, $\overline{F}_{CdSO_4}$, is 1,000 ±20 Int. joules greater in D_2O than in H_2O solutions whose concentration is

0.0602 mole $CdSO_4$ per mole of water at 20°C. From the constancy of the difference between the electromotive force of the saturated H_2O and D_2O cells and the small variation in concentration of the saturated $CdSO_4$ solutions over the range 17° to 28°C, the value calculated for the difference in partial molal free energy of $CdSO_4$ in H_2O and D_2O solutions is independent of temperature to within the limits of error of this calculation.

Since the cells on which these measurements were made contained a small amount of added H_2SO_4, this discussion strictly applies only to solutions which are 0.032 normal in H_2SO_4 and saturated with respect to Hg_2SO_4 (5.2×10^{-5} mole Hg_2SO_4 per mole of water [11]).

V. CONCLUSION

The substitution of D_2O for normal water in saturated standard cells affords a variation in the customary type of cell which appears to be equally as good as the best Weston normal cells, now used as a standard for the International volt. More experience with deuterium cells is doubtless required, but at the present time cells containing high percentages of D_2O seem to offer the best possibility of obtaining another type of cell which can be used as a primary standard. If several groups of different types of cells maintain the same relative values of electromotive force over long periods of time, the evidence that each group is constant is improved. The Bureau now depends on groups of acid and neutral Weston cells and hopes ultimately to employ the deuterium cells as a part of the standard.

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USE OF CHLORITES FOR TREATING RAW SUGARS

By Horace S. Isbell

ABSTRACT

The use of sodium and calcium chlorites for the bleaching of raw-sugar crystals and sugar sirups was investigated and a method for treating raw sugar was devised. Chlorites in neutral and slightly acid solutions exert a slow bleaching action on the colored impurities in raw sugar. In addition to the bleaching action, chlorites have marked bactericidal properties, so that treatment of raw sugars and sugar solutions with chlorites inhibits bacterial action. Inasmuch as pure sucrose is not altered by contact with chlorites at room temperature for long periods, the chlorite can remain in contact with the sugar crystals in storage and reduce the loss of sugar ordinarily caused by bacterial action.

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I. INTRODUCTION

Heretofore various chemicals—such as chlorine, sodium hypochlorite, chlorine dioxide, peroxides, and other reagents—have been used for bleaching sugars and sugar solutions, but these have not been wholly satisfactory. Recently the Mathieson Alkali Works has made commercially available a compound, sodium chlorite, which appears to have valuable properties as a bleaching agent.[1] Inasmuch as the literature did not reveal the chemical behavior of the simple carbohydrates with chlorites, the author, in collaboration with Allene Jeanes, undertook an investigation of the reactions of chlorites upon such diverse carbohydrate materials as pure sugars, sugar alcohols, aldonic acids, and glycosides.[2] In the present paper, experiments are reported to show the application of the new reagent in the treatment of raw sugars and sugar sirups.

The investigation has revealed that pure sucrose is not altered by contact with chlorites at room temperature for a period of over 100 days, and that in acid solution, chlorites have a marked bleaching action on the colored impurities in raw sugar. In neutral solution the bleaching action was found to be very slow and to require several days at room temperature. The bleaching action is rapid in acid solution, but since sucrose is hydrolyzed readily by acids at high temperatures, these conditions cannot be employed in a technological process. In

[1] M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, Ind. Eng. Chem. **32**, 899 (1940). M. C. Taylor, J. F. White, and G. P. Vincent, Techn. Assn. Papers, Series XXIII, No. 1 (1940).

[2] A. Jeanes and H. S. Isbell, J. Research NBS **27**, 125 (1941) RP1408.

spite of these inauspicious circumstances, a practical process for treating raw sugar was devised. In this process the slowness of the bleaching action is not objectionable because the bleaching agent is allowed to remain in contact with the raw sugar while it is in storage. In the early stages of this investigation it was noted that molds develop in sugar solutions which have not been bleached or which have been bleached with hypochlorites, but that molds do not ordinarily develop in solutions bleached with chlorites. The marked difference in the behavior of the solutions treated with hypochlorite and those treated with chlorite probably arises from the difference in the rates of reaction for the hypochlorite and chlorite. The hypochlorite reacts quickly with the organic material and is reduced to chloride, which has little or no bactericidal effect. Chlorites, however, react slowly and remain in solution for a long time and thus exert a prolonged bactericidal and fungicidal action. Because of this characteristic the addition of a chlorite to a raw sugar prevents the growth of bacteria and molds and at the same time results in a slow bleaching action.

II. TREATMENT OF CRYSTALLINE RAW SUGAR IN STORAGE

Ordinarily considerable time elapses between the production of raw sugar and its use at the refinery. During this period there is some loss of sucrose by the action of bacteria and molds, and consequently the addition of a bactericidal agent is advantageous. Spraying the raw-sugar crystals with a solution of sodium or calcium chlorite would introduce the bleaching agent into the film of molasses which coats the sugar crystals, and reaction would take place slowly during the storage period. Since the bacterial action takes place in the molasses film, the presence of the chlorite at this point would seem to be particularly opportune. In the refining process the raw sugar, which has been in storage for varying lengths of time, is affined (that is, mixed with water or sirup to make a magma and centrifuged). This removes the bulk of the impurities and a large portion of the color which is in the film of molasses coating the crystals. In the process contemplated the excess chlorite and buffer would be removed with the affination sirup and subsequently processed to yield light-colored sirups.

The experiments outlined in table 1 show the behavior of raw sugar when treated with chlorites, both in the absence and in the presence of buffering agents. In each experiment the raw sugar was thoroughly mixed with the chlorite and the other reagents in the proportions given. The mixture of raw sugar and reagents was transferred to a glass-stoppered bottle and was allowed to stand at room temperature in a dark place. At the designated times, samples of the sugar were taken and the intensity of the color (specific absorptive index) was determined with the simplified apparatus and by the method described by Brewster.[3] For comparison, each "absorptive index" was divided by the "absorptive index" of a sample of the sugar which had been mixed with a like quantity of water and allowed to stand for the same time. The values thus obtained are given in the column designated "relative absorptive index." The acidity of the crystalline raw sugar could not

[3] J. F. Brewster, J. Research NBS **16**, 349 (1936) RP878.

be determined directly, and consequently measurements were made with solutions prepared by dissolving 1 part of the sugar in 3 parts of water. The color of the raw sugar, after treatment with either sodium or calcium chlorite in acid solution, decreased perceptibly in the course of several hours, reaching a minimum in most cases in the course of several days. The decrease in color depends in large measure on the amount of chlorite added. In the experiments in which considerable chlorite was added, the bleaching action was accompanied by the evolution of chlorine dioxide; but when small quantities of chlorite were used, the presence of chlorine dioxide was not apparent.

TABLE 1.—*Treatment of crystalline raw sugar*

Experiment	100 g of raw sugar treated with the reagents listed below	Results after the sugar mixture had stood at room temperature for—								
		1 day			7 days			55 days		
		Specific absorptive index,[a] $-\log t$	Relative absorptive index[b]	Acidity,[c] pH	Specific absorptive index,[a] $-\log t$	Relative absorptive index[b]	Acidity,[c] pH	Specific absorptive index,[a] $-\log t$	Relative absorptive index[b]	Acidity,[c] pH
1	2 ml of H_2O	1.014	1.00	6.4	0.853	1.00	6.5	0.516	1.00	6.6
2	2 ml of 25% $NaClO_2$	0.266	0.26	5.3	.187	0.22	5.2	.307	0.59	5.2
3	1 ml of 25% $NaClO_2$+1 ml of H_2O	.301	.30	5.9	.374	.44	5.6	.376	.73	5.6
4	2 ml of 12.5% $Ca(ClO_2)_2$	.357	.35	5.6	.423	.50	5.5	.398	.77	5.2
5	1 ml of 25% $NaClO_2$, 1 ml of H_2O+2 g of solid $CaCO_3$	.494	.49	7.2	.492	.58	7.0	.424	.82	7.1
6	1 ml of 25% $NaClO_2$, 1 ml of saturated $NaHCO_3$ solution	1.325	1.31	8.7	.822	.96	8.0	.401	.78	6.8
7	0.3 ml of 12.5% $Ca(ClO_2)_2$, 1.5 ml of 4.9% $Ca(ClO)_2$	0.736	0.73	6.3	.787	.92	6.0	.491	.95	6.0
8	0.3 ml of 25% $NaClO_2$+2.25 ml of 4.9% $Ca(ClO)_2$	.840	.83	6.4	.866	1.02	6.2	.506	.98	5.9
9	0.15 ml of 25% $NaClO_2$+2.25 ml of 4.9% $Ca(ClO)_2$	.834	.82	6.4	.828	0.97	6.2	.513	.99	5.1

[a] The "specific absorptive index," $-\log t$, is the absorptive index of a solution of the sugar reduced to unit conditions regarding thickness and concentration. It is calculated from the equation $-\log t = -\log T/bc$, in which b is the thickness in centimeters of the absorbing solution, c is the concentration of the sugar in grams per milliliter, and T is the transmission of the standard plate as given by calibration at 560 mμ.

[b] The ratio of the "specific absorptive index" of the sugar mixture to the "specific absorptive index" of the sugar treated in like manner but without the addition of either chlorites or hypochlorites.

[c] The acidity of a solution containing 1 g of the sugar mixture dissolved in 3 g of water.

The addition of chlorite and the ensuing bleaching action usually leads to an increase in the acidity of the sugar mixture. This objectionable feature may be overcome by the addition of a base or buffer to the raw-sugar mixture. The buffer neutralizes any acid formed while the sugar is in storage, and thus lowers the loss of sugar by hydrolysis. The bleaching action is retarded by the addition of the base or buffer; but this retardation is immaterial, because ordinarily the sugar is kept in storage for a long time. Furthermore, the slower the reaction the longer the chlorite remains in contact with the sugar and protects it from bacterial action. In experiment 6, table 1, in which sodium bicarbonate was added, in addition to sodium chlorite, the color increased at first and then decreased slowly; after 55 days the specific absorptive index was 0.78 of that of the sugar in the control

experiment. Treatment of the sugar with a mixture of chlorite and hypochlorite (experiments 7, 8, and 9) caused a rapid decrease in color, but the bleaching effect was not so permanent as that obtained by the use of chlorites alone. After standing for 7 days, there was little difference in the appearance of the samples treated with the chlorite-hypochlorite mixtures and the appearance of the control sample.

The change in color given in table 1 is not an adequate measure of the value of the treatment. From a practical viewpoint the value of the treatment depends in part on the behavior of the sugar in the subsequent purification steps. Although the colored impurities which remain in the solutions after treatment with chlorites are easily removed by filtration over bone char, the discussion of this phase of the subject must await further investigation. In the technological application of the process, the raw sugar might be sprayed in the centrifugal with a solution containing the chlorite and buffer. This is a simple procedure, and does not require equipment or steps other than those ordinarily used in the production of sugar.

III. EXPERIMENTS WITH SUGAR SOLUTIONS

Although the method for treating raw sugar outlined in the preceding paragraph is very simple and convenient, in some cases it may be desirable to bleach sugar solutions or to conduct the bleaching operation at another stage in the manufacturing process. At most points in the process a very slow reaction would be objectionable, and hence a series of measurements was made with the purpose of ascertaining whether or not the rate of bleaching could be increased by increasing the acidity or by adding a hypochlorite in a manner analogous to the procedure already used for bleaching cellulose fibers (see footnote 1).

TABLE 2.—*Effect of acidity on the bleaching action of chlorites in raw-sugar solutions*

Time	100 g of sugar, 100 g of water, 1 g of $NaClO_2$			100 g of sugar, 100 g of water, 1 g of $NaClO_2$, 1.6 ml of 1 *M* H_3PO_4			100 g of sugar, 100 g of water, 1 g of $NaClO_2$, 0.4 ml of 1 *M* H_3PO_4			100 g of sugar, 100 g of water, 1 g of $NaClO_2$, 0.1 g of $NaHCO_3$		
	Acidity, pH	Specific absorptive index, $-\log t$	Relative absorptive index [a]	Acidity, pH	Specific absorptive index $-\log t$	Relative absorptive index [a]	Acidity, pH	Specific absorptive index, $-\log t$	Relative absorptive index [a]	Acidity, pH	Specific absorptive index, $-\log t$	Relative absorptive index [a]
Hours												
0.5	6.1	1.050	1.14	4.2	0.410	0.45	5.1	0.691	0.75	8.2	1.231	1.34
2	6.1	0.855	0.93	4.2	.115	.13	5.1	.587	.64	8.2	1.262	1.37
6	6.1	.753	.82	4.2	----	----	5.1	.450	.49	8.2	1.262	1.37
24	6.1	.608	.66	4.2	----	----	4.9	.193	.21	8.1	1.262	1.37

[a] The ratio of the "specific absorptive index" of the sugar mixture to that of the untreated raw sugar.

The results given in table 2 show that the bleaching of raw-sugar solutions with chlorites is more rapid in strongly acid solution than in weakly acid solution and that there is no appreciable bleaching in alkaline solution, as, for example, in the experiment in which sodium bicarbonate was added. The increase in the intensity of color noted in the sodium bicarbonate solution is largely caused by the alkaline reaction and disappears when the solution is made acid.

Upon the addition of sodium chlorite to a solution containing the raw sugar, the yellow-brown color increases slightly at first, but decreases on standing so that ultimately a decided bleaching action is obtained. The cause of the initial increase in color is not known, but a similar increase in color is found when raw sugar is treated with calcium hypochlorite (table 3).

TABLE 3.—*Treatment of raw-sugar solutions with chlorites in conjunction with hypochlorites at approximately 26° C*

100 g of sugar dissolved in 100 g of water plus the reagents indicated below			0.5 hour after addition of reagents		20 hours after addition of reagents		100 hours after addition of reagents	
$NaClO_2$	$Ca(ClO)_2$	1 *M* H_3PO_4	pH	Relative absorptive index [a]	pH	Relative absorptive index [a]	pH	Relative absorptive index [a]
g	*g*	*ml*						
0	----------	----------	6.2	1.00	----------	1.00	----------	1.00
0.5	----------	----------	6.2	1.12	----------	.83	5.7	0.40
1.0	----------	----------	6.1	1.14	----------	0.65	----------	----------
0.1	----------	0.8	4.8	0.92	4.8	.54	4.9	.41
.2	----------	.8	4.8	.84	4.8	.52	4.8	.25
.5	----------	.8	4.8	.79	4.8	.33	4.1	.03
----------	0.2	----------	6.9	1.31	6.6	.59	6.3	.62
----------	.6	----------	7.1	0.50	----------	.53	6.6	.60
----------	.1	.8	5.1	.92	5.0	.93	4.9	.95
----------	.2	.8	5.2	.81	5.1	.93	5.0	1.00
----------	.6	.8	5.7	.21	5.2	.47	5.0	0.52
.1	.1	----------	6.8	1.22	6.4	1.10	6.2	1.00
.1	.2	----------	7.0	1.25	6.4	1.12	6.2	0.89
.1	.4	----------	7.2	0.83	6.3	0.59	6.3	.48
.2	.2	----------	7.2	1.25	6.5	1.08	6.2	.69
.2	.4	----------	7.2	0.71	6.3	0.46	5.9	.25
.2	.6	----------	7.3	.15	6.1	.10	5.5	.05
.5	.2	----------	7.0	1.06	----------	.61	5.8	.24
.5	.4	----------	7.1	0.57	----------	.15	5.0	.03
.5	.6	----------	6.5	.22	----------	.12	4.7	.03
.05	.3	.8	5.5	.33	5.0	.57	5.0	.60
.05	.4	.8	5.5	----------	5.0	.46	4.9	.64
.1	.1	.8	5.0	.85	4.9	.65	4.9	.69
.1	.2	.8	5.3	.71	5.1	.46	5.0	.44
.1	.4	.8	5.4	----------	5.0	.25	5.0	.42
.2	.2	.8	5.0	----------	----------	.29	4.7	.13
.2	.3	.8	5.0	----------	----------	.16	4.7	.06
.2	.4	.8	5.4	----------	4.9	.08	4.9	.20
.5	.2	.8	5.4	.66	----------	.14	4.0	.03
.5	.4	.8	5.6	----------	----------	.07	3.9	.06

[a] The ratio of the "specific absorptive index" of the sample to that of the untreated raw sugar. The absorptive index ($-\log t$) of the untreated raw sugar was 0.919 at 560 mμ.

Table 3 gives the results obtained from a series of experiments in which different quantities of sodium chlorite, calcium hypochlorite, and phosphoric acid were added to raw-sugar solutions. The specific absorptive index of the solution treated with 0.5 g of sodium chlorite after 100 hours was 0.40 of that of the untreated sugar solution, whereas the specific absorptive index of a similar solution containing, in addition to the chlorite, 0.8 ml of 1 *M* phosphoric acid, was only 0.03 of that of the untreated sugar solution. The use of both sodium chlorite and calcium hypochlorite gives a more rapid bleaching effect in a more nearly neutral medium. Thus the specific absorptive index of the sample treated with 0.2 g of sodium chlorite and 0.6 g of calcium hypochlorite decreased in 0.5 hour to 0.15 of the original value, while

the acidity was pH 7.3. Although the bleaching effect of hypochlorites appears to be more rapid than the bleaching effect of chlorites, it appears to be less permanent. It is known that chlorites in aqueous solution react with hypochlorites to give chlorine dioxide. This substance is an excellent bleaching agent and may account for the rapid bleaching of raw sugars by a mixture of chlorite and hypochlorite. The bleaching action of chlorites may also be due in large part to the formation of chlorine dioxide, and the rate of bleaching may be determined by its rate of formation.

The results given in table 4 show the bactericidal and fungicidal effect of the addition of chlorites to a 50-Brix solution of raw sugar. The solutions were kept at room temperature in glass bottles under conditions favorable for the growth of bacteria and molds. An examination of the solutions after standing for 5 months revealed mycelia in all of the samples not treated with chlorites, while those treated with chlorites, with the exception of numbers 10, 11, and 12, failed to show visible growths. Concentrations of calcium hypochlorite six times as high as the concentrations found to be effective for sodium chlorite did not prevent the appearance of mold or bacterial growths. The lower bactericidal action of chlorites in the presence of hypochlorites and phosphoric acid, illustrated by the results of solutions 10, 11, and 12, may be explained by the interaction of the chlorite, hypochlorite, and acid, which removed the chlorite from solution and lowered the bactericidal effect.

TABLE 4.— *Inhibition of the formation of mold or bacterial growths by the addition of chlorites and hypochlorites to solutions of raw sugar*

Solution number	Reagents added to each 200 g of 50-Brix sugar solution			Condition of solution after standing for 5 months in glass-stoppered bottles at room temperature
	$NaClO_2$	$Ca(ClO)_2$	1 *M* H_3PO_4	
	g	*g*	*ml*	
1	0.1			No mycelium.
2	.1			Do.
3	.2		0.8	Do.
4	.5		.8	Do.
5	.1	0.1		Do.
6	.1	.2		Do.
7	.1	.4		Do.
8	.2	.2		Do.
9	.2	.4		Do.
10	.1	.4	.8	Mycelium present.
11	.05	.4	.8	Do.
12	.05	.3	.8	Do.
13		.6	.8	Do.
14		.2	.8	Do.
15		.1	.8	Do.
16		.2		Do.
17				Do

Although the experiments described in this paper show the possible usefulness of chlorites for treating raw sugars, the commercial application of chlorite in the refining of sugar might involve some complications which it may not be amiss to consider briefly. The most objectionable feature of the use of chlorites is the danger of fire or explosion. In this connection, the effect of chlorites on the spontaneous combustion of sugar and on the inflammability of sugar dust are

problems of importance. Furthermore, chlorites and chlorine dioxide are toxic compounds and might affect the health of the workers adversely. Hence the physiological effects of chlorites and chlorine dioxide should be investigated in order to ascertain safe working conditions. In the final analsyis the use of chlorites by the sugar industry will depend on whether or not their use can reduce the cost of producing refined sugar. This can be ascertained only by extensive investigation, closely coordinated with the sugar industry.

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STRUCTURE OF TRICALCIUM ALUMINATE

By Howard F. McMurdie

ABSTRACT

A review of the work on the structure of $Ca_3Al_2O_6$ is given. The present study shows that $Ca_3Al_2O_6$ has a cubic unit cell having $a_0 = 15.24$ A, and with 24 molecules present. By comparison with other compounds with similar patterns, it is seen that the metal atoms are arranged at or near the centers and corners of 3.81 A cubes. No deductions can be drawn about the oxygen arrangement from a consideration of the strong lines only.

Since there are many compounds which give patterns whose strong lines are those of a body-centered cube with 3.81 A edges, it is suggested that the pattern obtained by Brownmiller from slowly quenched glasses of portland cement compositions was the result of submicroscopic quench growths of metastable crystalline compounds.

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I. INTRODUCTION

Tricalcium aluminate ($Ca_3Al_2O_6$) was first identified as a distinct compound by Shepherd, Rankin, and Wright [1][1] in 1909. A few years later it was found [2] to be a product of complete crystallization at equilibrium in the system CaO-Al_2O_3-SiO_2, and from this study its occurence in portland cement clinker was predicted and subsequently verified. It is now believed to be present in many normal cement clinkers. The compound is acted upon rapidly by water, resulting in high early heat of hydration, and forms complex products with sulfates, which lower the resistance of concrete to the action of sulfate waters.

The importance of tricalcium aluminate in portland cement chemistry has resulted in several investigations to determine its crystal structure. No unique satisfactory solution of its structure, however, has yet been found. In the present paper the work on $Ca_3Al_2O_6$ is reviewed, comparisons are made with diffraction patterns of other compounds, and some deductions are drawn in regard to its possible structure.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. PREVIOUS WORK ON THE STRUCTURE OF $Ca_3Al_2O_6$

Tricalcium aluminate was found by Rankin and Wright [2] to be isotropic with an index of refraction of 1.710 and to melt incongruently at 1,455° C into CaO and liquid. The incongruent melting of $Ca_3Al_2O_6$ has made it difficult to prepare large single crystals, from which the determination of crystal class can be made by means of diffraction patterns.

Harrington [3] obtained powder diffraction patterns of $Ca_3Al_2O_6$ and concluded that it was "pseudocubic" with a unit cell having $a_0=7.62$ A. He found six lines in the pattern to which he was not able to assign cubic indices (with a cell of 7.62 A). The density indicated three molecules in this unit cell.

Steele and Davey [4] made the first attempt to find the atomic positions in the crystal. While these workers did not list the lines found by them in the pattern, they reported the cell as cubic, with $a_0=7.64$ A, and made no mention of any difficulty such as Harrington encountered in indexing certain lines. Steele and Davey postulated a structure in the space group O_h^1 which accounted in an approximate way for the observed intensities. This arrangement, which had one Ca atom with no surrounding O atoms and one group of six O atoms with no central cation, planary AlO_4 groups, and interatomic distances which seem unusual, appears unlikely, and consequently various workers have suggested changes.

Hermann's [5] method of producing a better balance of the valences, by placing together the extra Ca and the six O atoms, left unchanged the unusual interatomic distances.

Lagerquist, Wallmark, and Westgren [6] obtained additional powder patterns of $Ca_3Al_2O_6$ and of an isostructural compound $Sr_3Al_2O_6$. They concluded that $Ca_3Al_2O_6$ had a cubic cell with an edge of 15.22 A, twice that proposed by Steele and Davey with eight times its volume. This would give 24 molecules in a unit cell. This unit cell was confirmed by Brady and Davey [14]. Büssem and Eitel [7] made Laue diagrams of the isostructural $Sr_3Al_2O_6$ and concluded that the symmetry was T_h. Beyond this no definite information is available. Since a similarity in pattern was found by Büssem between perovskite ($CaTiO_3$) and $Ca_3Al_2O_6$, he considered that $Ca_3Al_2O_6$ must have a perovskite structure and speculated on possible atomic positions.

III. STRUCTURAL RELATIONS OF $Ca_3Al_2O_6$ TO OTHER COMPOUNDS

The diffraction data for $Ca_3Al_2O_6$ obtained in this laboratory are given in table 1.[2] This material was prepared by heating 62.2 percent of CaO and 37.8 percent of Al_2O_3 just below 1,450° C for 4 hours. The material was then ground and reheated. This was repeated until petrographic examination indicated that the sample contained over 95 percent of one phase. These diffraction data indicate a cubic unit cell with $a_0=15.24$ A, in agreement with the findings of Lagerquist and coworkers. On the basis of this cell all the observed lines were indexed, including several first-order lines which could not result from a unit cell with $a_0=7.62$ A.

[2] In all patterns made for this paper, CuKα radiation was used with cylindrical cameras having a radius of about 5.7 cm.

TABLE 1.—*Powder diffraction data on* $Ca_3Al_2O_6$

[Cubic $a_0 = 15.24 \pm 0.02$ A]

[*VS*=very strong; *VW*=very weak; *M*=medium; *S*=strong; *W*=weak]

Estimated intensity	*d*	*hkl*	Estimated intensity	*d*	*hkl*
W	4.08	123	*VW*	1.951	650-643
VW	3.34	124	*S*	1.907	800
VS	2.70	440	*VW*	1.826	653
W	2.39	620	*S*	1.556	844
VW	2.258	630-542	*M*	1.346	880
M	2.200	444	*M*	1.206	12.40
VW	2.039	642	*W*	1.106	888
VW	1.984	731-553	*M*	1.023	12.84

Examination of these data revealed that the stronger lines considered alone defined a body-centered cubic structure with $a_0 = 3.81$ A. A similarity between these strong lines and those of other compounds has been noted by several workers. Büssem [7] found that perovskite ($CaTiO_3$) had strong lines at the same positions as those of $Ca_3Al_2O_6$, and Brownmiller [8], in a study of the system CaO-Na_2O-Al_2O_3, showed that the powder diffraction pattern of $NaCa_4Al_3O_9$ was also similar.

In the present investigation it has been found that the compounds of the cristobalite type [9] give a similar series of strong lines. Included in this group of compounds are high cristobalite (SiO_2), alpha carnegieite ($NaAlSiO_4$), and Na_2CaSiO_4. The strong lines of the last compound are most similar to those of $Ca_3Al_2O_6$. $Na_4Ca(SiO_3)_3$ and $Na_2Ca_3(SiO_3)_3$ also have a series of strong lines somewhat similar to those of $Ca_3Al_2O_6$ [10].

From a consideration of the similarity of the strong lines of the pattern of $CaTiO_3$, Na_2CaSiO_4, and $Ca_3Al_2O_6$, it may be assumed that they have some structural characteristics in common. Previous investigations [9, 11] have reported complete structural analyses for $CaTiO_3$ and Na_2CaSiO_4. A comparison of these two known structures would be expected to reveal what they had in common that caused the strong lines of a body-centered lattice with $a_0 = 3.81$ A. In this way the similar strong lines in the pattern of $Ca_3Al_2O_6$ might be explained.

TABLE 2.—*Powder diffraction data on* $CaTiO_3$

[Cubic $a_0 = 3.82 \pm 0.02$ A]

[*VS*=very strong; *VW*=very weak; *M*=medium; S=strong; *W*=weak]

Estimated intensity	*d*	*hkl*	Estimated intensity	*d*	*hkl*
W	3.8	100	*VW*	1.286	300-221
VS	2.70	110	*M*	1.207	310
W	2.20	111	*VW*	1.099	222
S	1.905	200	*W*	0.9562	400
VW	1.710	210	*S*	.9001	411-330
S	1.558	211	*VW*	.8755	331
M	1.348	220	*M*	.8560	420

The diffraction data for $CaTiO_3$ are given in table 2. These data indicate a cubic unit cell with $a_0 = 3.81$ A. The lines with $h+k+l=2n$ (those of a body-centered lattice) are the stronger. Barth [11] showed that this compound has one molecule to the unit cell and arrived at a

structure with a Ti atom at the center and a Ca atom at each corner of the unit cell. Both the Ca and Ti atoms contribute to the strength of the reflections from planes with $h+k+l=2n$, whereas the reflections from these atoms are out of phase in other planes. This would cause the lines representing a body-centered pattern to be relatively strong. Since the oxygen atoms are placed at 1/2 1/2 0, 1/2 0 1/2, and 0 1/2 1/2, the Ti atom is surrounded by 6 and the Ca atom by 12 equally distant O atoms.

The diffraction data for Na_2CaSiO_4 given in table 3 represent a cubic compound with $a_0=7.62$ A. It is found that here, as in $CaTiO_3$, the strong lines are those of a body-centered cube with $a_0=3.81$ A. Barth and Posnjak [9] worked out the atomic positions in this structure and found that with four molecules per cell, Na, Ca, and Si atoms were at or near the corners and centers of cubes representing one-eighth of the full cell. Here again, as in $CaTiO_3$, all heavy atoms contribute to reflections of planes which could result from a body-centered cube of 3.81 A, while the reflections from these atoms are out of phase in other planes. The oxygen arrangement in this compound is completely different from that of $CaTiO_3$. In Na_2CaSiO_4 both Si and Ca atoms are surrounded tetrahedrally, and these groups form chains by the sharing of common O atoms. This is a structure derived from that of high cristobalite by the substitution of Ca atoms for Si and the placing of Na atoms in the large open spaces.

TABLE 3.—*Powder diffraction data on* Na_2CaSiO_4

[Cubic $a_0=7.58$ A]

[*VS*=very strong; *VW*=very weak; *M*=medium; *S*=strong; *W*=weak]

Estimated intensity	*d*	*hkl*	Estimated intensity	*d*	*hkl*
S	4.38	111	*M*	1.327	440
VW	3.79	200	*W*	1.269	531
VS	2.68	220	*M*	1.186	620
M	2.170	222	*VW*	1.141	533
S	1.879	400	*VW*	1.083	444
S	1.533	422	*VW*	1.049	711-551
W	1.444	511-333	*M*	1.001	642

From the above discussion it is evident that $CaTiO_3$ and Na_2CaSiO_4 have a cation arrangement in common, consisting of relatively heavy atoms at or near the corners and centers of cubes with an edge of 3.81 A. The strong lines of the powder diffraction pattern of both compounds are therefore those of a body-centered cube with $a_0=3.81$ A. However, the important and differentiating aspects of the structure, namely, the oxygen coordination of the cations, are not shown by these strong lines.

From similarities of the positions of strong lines in the patterns of $CaTiO_3$ and Na_2CaSiO_4 with those in the pattern of $Ca_3Al_2O_6$, it may be assumed that $Ca_3Al_2O_3$ also has a similar structure, with relatively heavy atoms (in this case Ca and Al) at or near the centers and corners of 3.81 A cubes. From the similarity of these lines alone, however, no deductions can be made in regard to the oxygen arrangement.

Harrington [3] found that a density determination indicated three molecules of $Ca_3Al_2O_6$ in a cell with $a_0=7.62$ A. In the cell with $a_0=15.24$ A there are 8×3, or 24, molecules. This would give 72

Ca, 48 Al, and 144 O atoms. Since there are 64 of the 3.81 A cubes in a full unit cell, there must be some vacant spaces, because the total of Ca and Al atoms lacks eight of filling all corner and center points.

A confirmation of this placing of the metallic atoms is found by a comparison of intensities of certain similar lines in the patterns of $Sr_3Al_2O_6$ and $Ca_3Al_2O_6$, compounds which appear to be isostructural. The diffraction data pertaining to $Sr_3Al_2O_6$ are given in table 4. In this pattern, made under conditions identical with those pertaining to the pattern of $Ca_3Al_2O_6$, it is seen, for example, that the 400 and 840 reflections are strong enough to register, while they do not appear in the pattern of $Ca_3Al_2O_6$. An arrangement of the heavy atoms as outlined above would give such a result. To account for this, consider 48 Al atoms and 16 Ca (or Sr) atoms at the centers of the 64 small cubes (such positions in the full cell as 1/8 1/8 1/8, 1/8 3/8 5/8, 5/8 7/8 1/8, etc.). The other 56 Ca (or Sr) atoms are then at corners of the small cubes (such positions as 0 0 0, 1/4 1/2 3/4, 3/4 1/2 0,etc.). Since the contribution of the oxygen atoms to the intensities would be very similar in both $Ca_3Al_2O_6$ and $Sr_3Al_2O_6$, let us consider only the contribution of the heavy atoms. The intensity factor, then, for the 400 and 840 planes would be

$$56\overline{R}-16\overline{R}+48\overline{Al},$$

where $\overline{R}$ is the F (scattering power) value for Ca or Sr atoms and $\overline{Al}$ is the F value for Al atoms for the particular reflection involved.

TABLE 4.—*Powder diffraction data on* $Sr_3Al_2O_6$

[Cubic a_0=15.82 A]

[*VS*=very strong; *VW*=very weak; *M*=medium; *S*=strong; *W*=weak]

Estimated intensity	*d*	*hkl*	Estimated intensity	*d*	*hkl*
W	5.6	220	*VW*	1.868	822-660
VW	4.3	123	*W*	1.773	840
VW	3.96	400	*VW*	1.684	664
VW	3.48	124	*VS*	1.616	844
VS	2.81	440	*S*	1.400	880
M	2.50	620	*W*	1.317	884-1200
M	2.28	444	*W*	1.285	10.64
M	2.111	642			12 22
S	1.975	800	*S*	1.254	12.40

The F values of Al and Ca are very nearly the same, so that the intensity resulting from the metal atoms would be rather small in $Ca_3Al_2O_6$ compared with that in $Sr_3Al_2O_6$, since the scattering power of Sr is about three times that of Al.

In a preceding paragraph it was shown that no conclusions can be drawn concerning the oxygen arrangement in $CaTiO_3$ and Na_2CaSiO_4 from a consideration of the strong lines in their diffraction patterns. It may be that the oxygen arrangement in $Ca_3Al_2O_6$ is not like that in either of these compounds. This would appear probable when it is noted that in a 3.81 A cube of $CaTiO_3$ there are three O atoms, while in Na_2CaSiO_4 there are only two and in $Ca_3Al_2O_6$ there are two and a quarter O atoms in the same volume.

Brandenberger [12] has classified cations as: (1) active, having low coordination numbers, such as Si and Al; and (2) inactive, with large coordination numbers, such as Na. Structures with both classes are made up of oxygen polyhedrons surrounding cations of

the first class, while cations of the second class complete the valence saturation and are placed in the large spaces with high oxygen coordination. If the activity of the calcium atoms of $Ca_3Al_2O_6$ is considered, especially with regard to action with water, it is probable that in this compound, as in Na_2CaSiO_4, the Ca atoms, in part at least, are of the first, or active, category and have low oxygen coordination.

IV. STRUCTURE OF GLASS IN PORTLAND CEMENT CLINKER

Brownmiller [13] prepared a series of mixtures having compositions near those of the liquids present during the heating of portland cement clinker. These mixtures all contained the oxides CaO, SiO_2, and Fe_2O_3, and in addition some had Al_2O_3. He then quenched small charges of melts of these various mixtures at two different rates. The faster quench, called instantaneous, gave in all cases isotropic products which produced no X-ray diffraction patterns. The slower quench, in which the charge stayed on the surface of the mercury and the cooling was considerably slower than in the first method, gave isotropic products, of higher index of refraction than the correspondingly fast quench. Microscopic examination of the slowly quenched material failed to reveal the presence of any crystal phases. This material produced an X-ray powder pattern consisting of the strong lines of $Ca_3Al_2O_6$. This same pattern was obtained by him even in those mixtures in which no Al_2O_3 was present. The pattern, reproduced in this laboratory by similar methods, had sharp, but in most cases rather weak, lines.

Brownmiller considered this material, which gave the pattern, to be a "metastable phase." By this he indicated a structure lacking the complete randomness of glass but still having some degree of irregularity.

It would seem impossible to have sharp lines resulting from a structure with any degree of randomness. Even if the structure consisted of an oxygen network with the other atoms at random, as described by Brownmiller, the different interatomic distances Fe-O, Ca-O, Si-O, and Al-O would result in a low degree of periodicity and a pattern consisting of broad lines.

Therefore, it seems more probable that the patterns in these slowly quenched samples are not the result of a semiglass material but of submicroscopic quench growths of a crystal phase. The identity of this phase is not known, but in this present work various compounds have been mentioned which give similar strong lines and doubtless others exist. Also, it is known that at high temperatures compounds form and can exist which would not be present at equilibrium conditions at lower temperatures. It is quite possible that there exists such a compound as $Ca_3Fe_2O_6$ which would very likely be isostructural with $Ca_3Al_2O_6$.

From the above considerations it seems very probable that the pattern obtained by Brownmiller from slowly quenched glasses is not due to a pseudocrystalline arrangement but to submicroscopic quench growths of a metastable compound.

V. SUMMARY AND CONCLUSIONS

The previous work on the structure of $Ca_3Al_2O_6$ was reviewed.

The present work confirms the findings of Lagerquist and coworkers that $Ca_3Al_2O_6$ has a cubic unit cell with $a_0=15.24$ A.

The strong lines of the diffraction pattern are those of a body-centered cube with $a_0=3.81$ A. These were shown to be caused by an arrangement of metal atoms at or near the corners and centers of 3.81 A cubes.

A comparison of the known structure of other compounds, which also show strong lines of a body-centered 3.81 A cube shows that no possible deductions can be drawn concerning the oxygen arrangements from a consideration of these strong lines.

Since there are many compounds which give patterns whose strong lines are those of a body-centered cube with $a_0=3.8$ A and since a structure which has any degree of randomness will not give a pattern with strong lines, it is suggested that the pattern obtained from slowly quenched glass of portland cement materials is caused by submicroscopic quench growths of a metastable crystalline compound.

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THE CARBOHYDRATE CONTENT OF COLLAGEN

By John Beek, Jr.

ABSTRACT

Colorimetric methods are used to study the carbohydrate in preparations of collagen made from hide, tendon, and bone. It was found that the three preparations all contain the same amount of the same kind of carbohydrate. This result confirms the indication of other experiments, namely, that the white fibrous connective tissues of hide, tendon, and bone are chemically identical. The color reactions of the collagen did not correspond exactly to those of any one or mixture of two of the known sugars studied, but they were similar to the reactions of a mixture of glucose and galactose. An attempt to ferment the carbohydrate in the hydrolyzate with galactose-active yeast showed that neither free *d*-glucose nor free *d*-galactose is present. A concentrate of the carbohydrate, prepared by the method described by Rimington, gave color reactions corresponding closely with those of a mixture of glucose and galactose. It appears, then, that the carbohydrate is combined through some difficultly hydrolyzable linkage, or that it is composed of *l*-glucose and *l*-galactose.

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I. INTRODUCTION

In an investigation now in progress, some properties of the white fibrous connective tissues of the hide, tendons, and bones of a steer are being compared. Measurements of combination with acid and with base [1],[1] and of electrophoretic mobility [2] gave evidence that in the natural state the white fibrous connective tissues from the three structures are chemically identical. In this paper colorimetric measurements of the carbohydrate content of the three preparations of collagen are described, together with some experiments giving information about the qualitative composition of the carbohydrate.

II. MATERIALS AND METHODS OF MEASUREMENT

The procedure used in preparing the collagen was essentially that recommended by Highberger [3]. The slight modifications that were necessary are given in an earlier publication [1]. Solutions for sam-

[1] Figures in brackets refer to list of references at end of this paper.

pling were made by hydrolyzing the collagen with dilute sulfuric acid.

The rare sugars used were made available through the courtesy of the Polarimetry Section of the National Bureau of Standards. The gulose was in the form of its addition compound with calcium chloride. All the other sugars used were in the pure crystalline form.

All the measurements were based on the color reactions of sugars with orcinol or α-naphthol. The first measurements were made according to the procedure worked out by M. Sørensen and G. Haugaard [4]. The method depends on the rate of development of color when a solution containing 40 mg of orcinol and not more than 0.2 mg of carbohydrate in 18 ml of 64-percent sulfuric acid is heated at 80° C. Sørensen and Haugaard recommended that the transmittancies at 430 and 530 mμ of solutions heated for six different periods of time up to 30 minutes be measured. The behavior of the ratio of the two corresponding absorbencies as the heating is continued is used to determine the qualitative composition of the carbohydrate. For this series of measurements in the present investigation, the sources of illumination were a mercury arc with filters designed to isolate the lines at 436 and 546 mμ, and an incandescent lamp with a filter transmitting a band with its center at 501 mμ. The transmittancy[2] of cells 1 cm thick was measured with a Martens photometer. Serious difficulty was encountered in making the measurements for the solutions that were heated for short periods of time, since the results were very sensitive to changes in the conditions of the reaction, and the colors obtained were fugitive. As it was not convenient to make the arrangements necessary for the satisfactory application of this method, it was decided to study the transmittancy over most of the visible spectrum of solutions prepared according to the Sørensen and Haugaard procedure, using 20 minutes for the time of heating. The reference solutions contained quinol in place of orcinol. Quinol was the only phenol among those tried that gave no color reaction with sugars. A Coleman Regional Spectrophotometer was used for the measurements.[3]

The results obtained by these two methods were still insufficient to establish the nature of the carbohydrate in collagen, and thus could not give its amount. Two effects in particular were desired that had not been obtained. One was a sharp distinction between the shapes of the curves obtained with glucose and galactose; the other was an increased absorption in the region of longer wavelengths, where the measurements are more precise and where discoloration of the protein during hydrolysis or during the reaction would be expected to interfere less. It was found that by using sulfuric acid at a higher concentration and permitting the reaction to take place at 25° C, red solutions were obtained which had transmittancies much higher in the blue and much lower in the yellow. In addition, the difference between glucose and galactose was somewhat more marked than with the solutions that were heated. The most favorable concentration of sulfuric acid was found to be 73 percent. The solutions were

[2] The transmittancy is the ratio of the intensity of the light transmitted by two solutions that are illuminated with light of the same intensity. The two solutions differ only in the absence from the reference solution of the substance being investigated. The absorbency is the negative common logarithm of the transmittancy. For the purpose of the present work, the absorbency was corrected for the effect of the reagents by subtracting the absorbency obtained with blank solutions, containing all components of the experimental solutions except the sugar or collagen.

[3] The use of this instrument was made possible through the cooperation of the Office of Forest Pathology of the Bureau of Plant Industry, U. S. Department of Agriculture.

allowed to stand 20 hours before the measurements were made, and quinol was used in the reference solutions.

Another color reaction of sugars with orcinol was investigated and modified for some further measurements. About 0.2 mg of sugar was allowed to react with 20 mg of orcinol and 1.4 mg of ferric chloride in about 18 ml of 36-percent hydrochloric acid. The solutions were allowed to stand for 3 days at 25° C. It was found later that although the absorbencies were less, a shorter time of reaction gave a better distinction between glucose and galactose. The solutions obtained were green, with a maximum absorbency at about 675 mμ.

The color reactions of several other phenols were tested to determine their applicability to this problem, but α-naphthol was the only

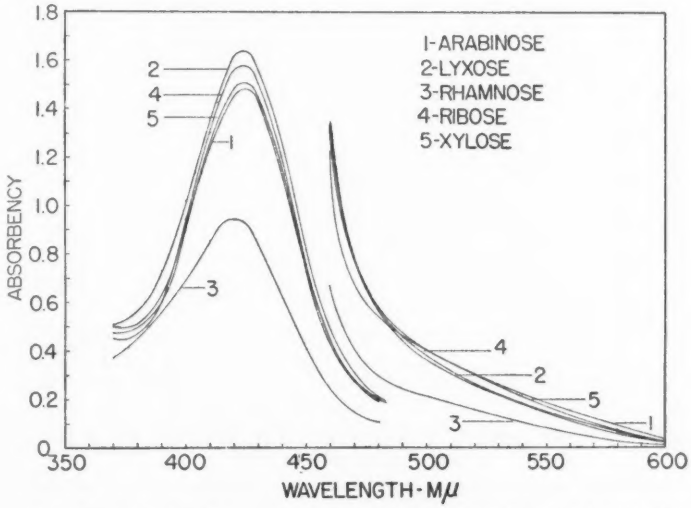

FIGURE 1.—*Spectral absorbency obtained with the aldopentoses and with rhamnose, after heating with orcinol.*

The solutions were diluted threefold before making the measurements at low wavelengths.

substance that was found to be useful. The conditions for the reaction with α-naphthol were like those used with the orcinol solutions that were heated, except that the temperature was 100°C. The transmittancies were measured with reference to water.

III. RESULTS

The spectral absorbency of a series of sugars and of hide collagen heated with orcinol [4] is shown in figures 1 and 2. The collagen solution contained the hydrolyzate from 34 mg of dry collagen. The measurements in the region of short wavelength (represented by the separate branches at the left of figs. 1 and 2) were made with solutions diluted to three times the original volume. It is apparent that only glucose and galactose, in this group of sugars, can be present in any considerable quantity in the carbohydrate in collagen. This result is in accord

[4] In order to avoid repetitive use of the expression "solution containing the products of the reaction of sugar (or collagen) with phenol in a strongly acid medium," the phrase "sugar (or collagen) with phenol" will be substituted.

with the report of Grassmann and Schleich [5] that the carbohydrate is composed of equal quantities of glucose and galactose. However, when an attempt was made to represent the absorbency of the collagen with orcinol as a multiple of the average for glucose and galactose, the result was not satisfactory. Table 1 gives the ratio of the absorbency for collagen to the average for glucose and galactose at a few wavelengths. The variation of this ratio is greater than the uncertainty of the measurement. If it is ascribed to the influence of the protein hydrolyzate on the formation of the colored substances, it

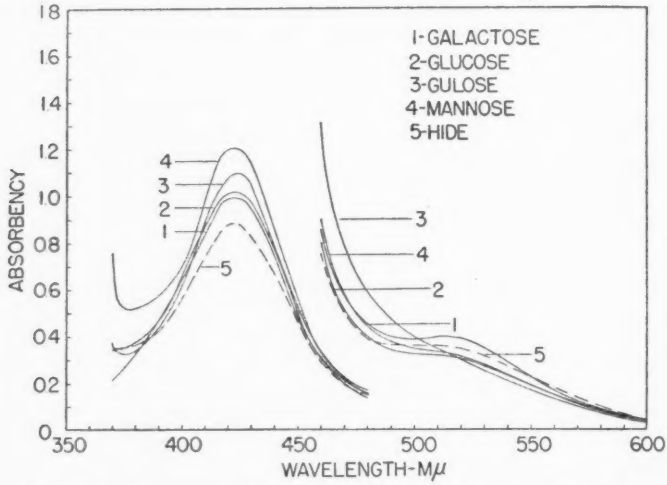

FIGURE 2.—*Spectral absorbency obtained with four aldohexoses and with hide collagen, after heating with orcinol.*

The solutions were diluted threefold before making the measurements at low wavelengths.

must be supposed that the effect is to decrease the amount of substance absorbing in the blue relative to the amount absorbing in the yellow.

TABLE 1.—*The ratio of the absorbency of collagen heated with orcinol to that of a mixture of equal amounts of glucose and galactose heated with orcinol*

Wavelength	$\frac{2\ (\text{Collagen})}{(\text{Glucose})+(\text{Galactose})}$
mμ	
560	1.12
520	1.01
480	0.93
440	.88
400	.89

The comparison between the collagens from the different sources was made directly by measuring the relative transmittancy of solutions heated with orcinol. All three comparisons were made by measurements in duplicate at 10 wavelengths. The differences in absorbency are shown in the second, third, and fourth columns of table 2. The fifth column gives the average of the three differences, which would be zero if the measurements were without error. Adjusted values of the differences were obtained by subtracting the

figures in the fifth column from those in the preceding three. These adjusted values were used in conjunction with the absorbency of solutions of hide heated with orcinol to calculate the ratio of the concentration of carbohydrate in the solutions of tendon and bone to that in the solution of hide. The results are shown in the last two columns of table 2.

TABLE 2.—*A comparison of the carbohydrate contents of solutions of hide, tendon, and bone, using the absorbencies of solutions heated with orcinol*

[*H*, *T*, and *B* denote absorbencies obtained with hide, tendon, and bone, respectively. The concentration of collagen is slightly different in the three solutions.]

Wavelength	*H*−*T*	*T*−*B*	*B*−*H*	Sum/3	*T*/*H*	*B*/*H*
mμ						
550	0.033	−0.035	0.004	0.001	0.86	1.01
540	.049	−.044	.005	.003	.83	1.01
530	.062	−.059	.006	.003	.81	1.01
520	.066	−.062	.006	.003	.82	1.01
510	.060	−.066	.005	.000	.83	1.01
500	.057	−.060	.002	.000	.84	1.01
490	.050	−.056	−.006	−.004	.85	0.99
480	.054	−.055	−.008	−.003	.85	.99
470	.064	−.060	−.014	−.003	.87	.98
460	.074	−.084	−.032	−.014	.88	.98

The average values of *T*/*H* and *B*/*H* are 0.85 and 1.00, respectively. The corresponding ratios of the weights of the samples are 0.90 and 1.02. Thus the apparent ratios of the concentrations of carbohydrate in the tendon and in the bone to that in the hide are 0.94 and 0.99.

A similar comparison of tendon and hide was made, using the solutions prepared in sulfuric acid at 25° C. The ratio obtained in this case was 0.97, the fluctuations being somewhat less than those in table 2.

In view of the small variations in the ratios shown in table 2, and of the small differences between the values obtained for the three preparations, it may be concluded that all three contain the same amount of the same kind of carbohydrate. The addition of this confirmatory evidence to that cited in the introduction makes possible the further conclusion that the white fibrous connective tissues of the hide, tendon, and bone of the steer are chemically identical.

The uncertainty about the qualitative composition of the carbohydrate mixture leaves some uncertainty about the quantity present. Although all the aldohexoses measured give approximately the same absorbency at 425 mμ, the measurements are subject to greater errors in this region of the spectrum, and it is also in this region that the protein hydrolyzate interferes most strongly with the measurement. The other colorimetric methods described in the experimental section were used to obtain information about the composition of the carbohydrate.

Figures 3, 4, and 5 show the curves for some known sugars, galacturonic acid, and hide collagen with sulfuric acid at 25° C. The curve for collagen corresponds fairly well to that for a mixture of equal quantities of glucose and galactose, but the smaller absorption in the blue still persists.

Figures 6 and 7 show the curves for several known sugars and hide collagen with hydrochloric acid and ferric chloride. Here the results

for collagen are intermediate between those for glucose and galactose, but the apparent proportion of glucose is larger than that indicated by the other experiments.

Figure 8 shows the transmittancies (referred to water) of glucose, galactose, and hide collagen with α-naphthol. The shape of the

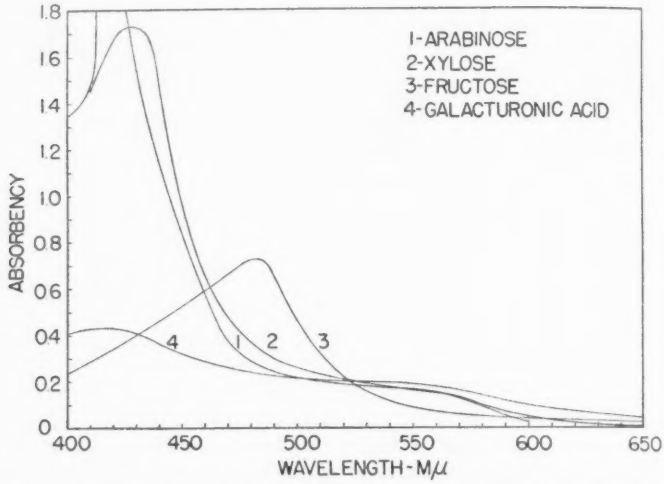

FIGURE 3.—*Spectral absorbency obtained with three sugars and with galacturonic acid, after reaction with orcinol at 25° C.*

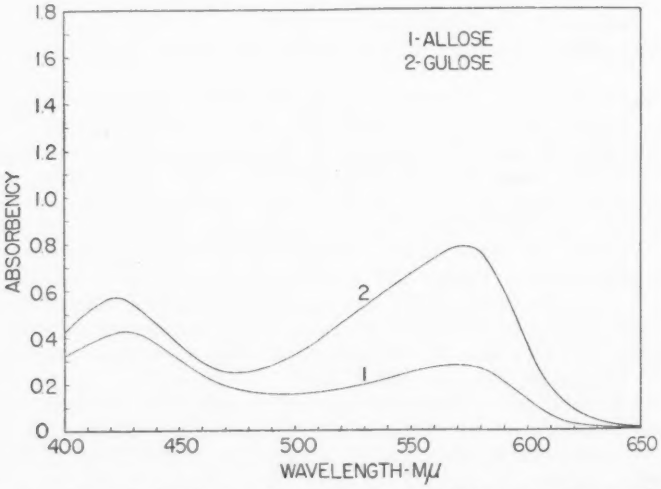

FIGURE 4.—*Spectral absorbency obtained with two aldohexoses after reaction with orcinol at 25° C.*

curve for collagen corresponds to that for a mixture of glucose and galactose.

If the carbohydrate could be removed from the hydrolyzate, the interfering effect of the noncarbohydrate material could be determined by adding a known sugar and then carrying out the color reaction.

It was suggested by H. S. Isbell, of the Polarimetry Section of the National Bureau of Standards, that a convenient way to destroy the carbohydrate without otherwise affecting the hydrolyzate would be to

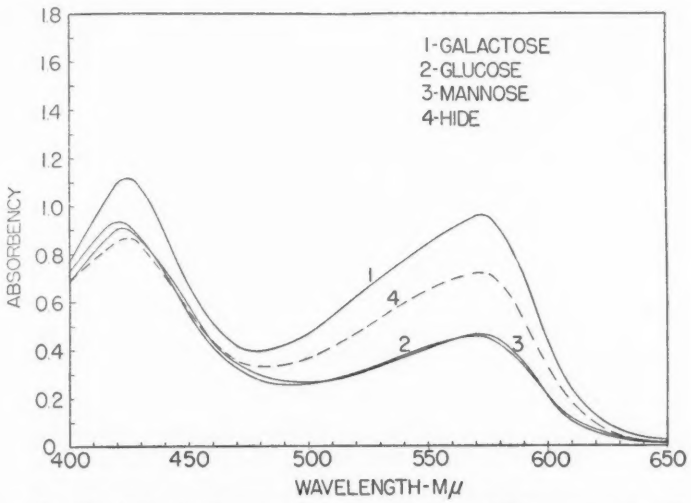

FIGURE 5.—*Spectral absorbency obtained with three aldohexoses and with hide collagen, after reaction with orcinol at 25° C.*

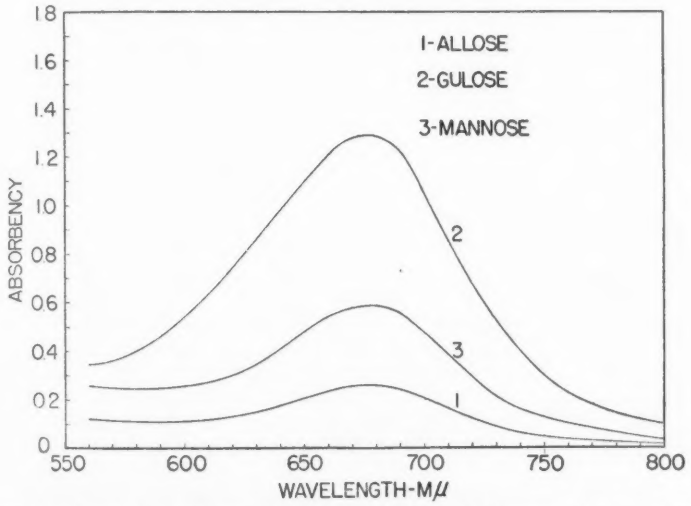

FIGURE 6.—*Spectral absorbency obtained with three aldohexoses after reaction with orcinol and ferric chloride.*

ferment the sugars with galactose-active yeast, provided, of course, that the carbohydrate is made up of *d*-glucose and *d*-galactose. Galactose-active yeast was prepared by a method similar to that of Kirby and Atkin [6]. Four successive cultures of yeast were grown in solu-

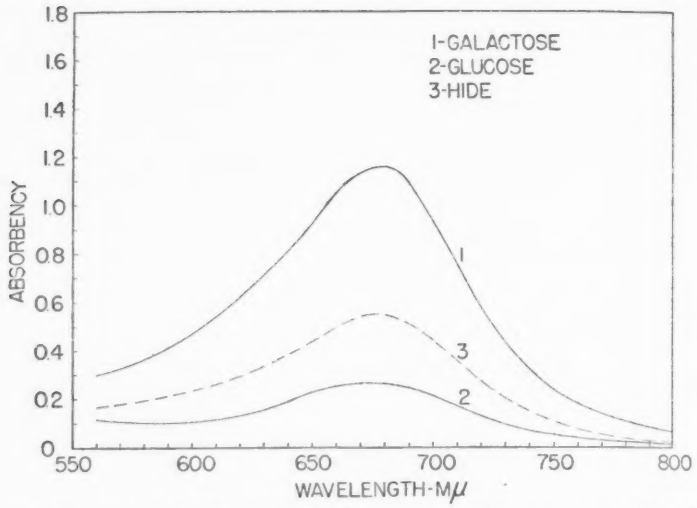

FIGURE 7.—*Spectral absorbency obtained with two aldohexoses and with hide collagen, after reaction with orcinol and ferric chloride.*

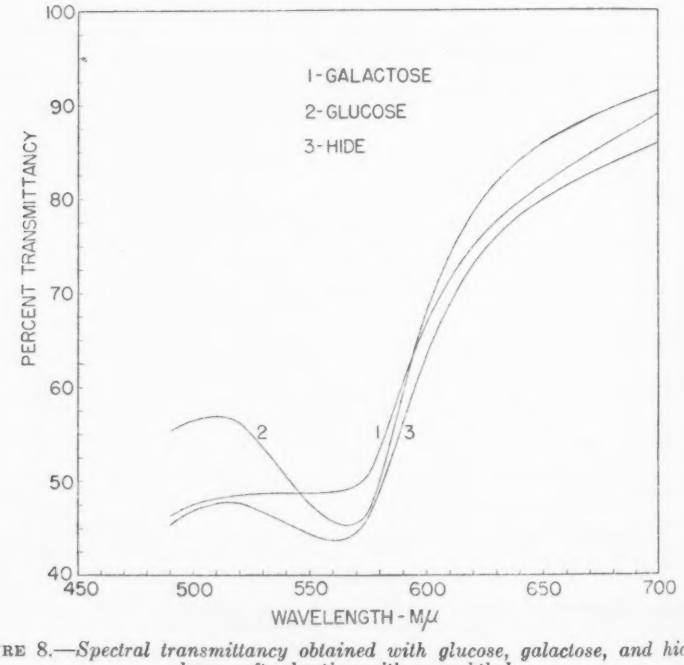

FIGURE 8.—*Spectral transmittancy obtained with glucose, galactose, and hide collagen, after heating with α-naphthol.*

tions containing *d*-glucose and *d*-galactose. The final product was washed with nutrient solution by centrifugation.

An attempt was made to ferment the sugar in a neutral solution of hydrolyzate, but the sugar was not fermented. In order to make sure

that the yeast was active in the solution in question, experiments were carried out in which *d*-galactose and yeast were added to hydrolyzed hide and bone collagens. In both cases the *d*-galactose was fermented and the sugar from the collagen remained. Table 3 gives the transmittancies of hide collagen and orcinol at 25° C with and without added galactose, after incubation with galactose-active yeast at 25° C for 4 days. The amount of galactose added was approximately equivalent to the carbohydrate in the collagen.

TABLE 3.—*The percentage transmittancies of collagen hydrolyzate with orcinol with and without added d-galactose, after incubation with galactose-active yeast*

Wavelength	Hide collagen+*d*-galactose	Hide collagen
mμ		
650	95.4	95.1
600	54.1	56.6
570	25.4	28.0
550	29.4	31.5
500	44.0	44.4
480	47.5	47.0
450	27.8	26.2
420	10.8	9.6

As the carbohydrate in the hydrolyzed collagen was not fermented, its identity was not established. If the sugar could be separated from most of the hydrolyzate, it might be expected that interference with the color reactions would be decreased. Rimington [7] has given a method for concentrating the carbohydrate complex in proteins, and Schneider [8] has shown that the method is applicable to collagen. Accordingly, the first precipitation of Rimington's method was carried out, using as the starting material 300 g of American standard hide powder. Measurements were made on the product with orcinol in sulfuric acid at 25° C, and with orcinol and ferric chloride in hydrochloric acid. The results are shown in figure 9. The curves in this figure represent the results calculated for a mixture of equal parts of glucose and galactose. The agreement between the two sets of results is close, and this agreement is significant because the ratio of the absorbency for galactose to that for glucose covers such a wide range. The ratio is 1.2 at 420 mμ and 2.1 at 570 mμ with sulfuric acid, and 4.4 at 680 mμ with ferric chloride and hydrochloric acid. It may be concluded, then, that these results confirm the report of Grassmann and Schleich [5], although a more certain determination of the composition of the carbohydrate might be desired. The color reactions and the resistance to fermentation indicate either that the carbohydrate is bound by a very difficultly hydrolyzable linkage or that it is composed of *l*-glucose and *l*-galactose. Bell and Baldwin [9] recently reported finding *l*-galactose in the tissues of a common edible snail.

The amount of carbohydrate in the collagen may be calculated on the assumption that it is composed of equal parts of glucose and galactose. The experimental results are better explained on the whole by supposing that the ratio of galactose to glucose is about 3 to 2, but the greater a priori likelihood of the ratio 1 to 1 makes its use seem more reasonable. The measurements in the neighborhood of 570 mμ with sulfuric acid at 25° C were used for the calculation, because these measurements are most likely to be free from the effects

of interference. The result for the hide collagen is 0.029 millimole of hexose per gram of dry collagen, which corresponds to 0.52 percent of monosaccharide, or 0.47 percent of carbohydrate residue, assuming that one molecule of water is eliminated in attaching each hexose residue. It may be pointed out that 0.029 millimole per gram gives a unit weight of about 34,000, which is approximately the unit weight found for the globular proteins. The coincidence is interesting even if not significant.

The form of the curves in figures 4 and 5 suggests the possibility that two colored substances are formed at different rates in the reaction of

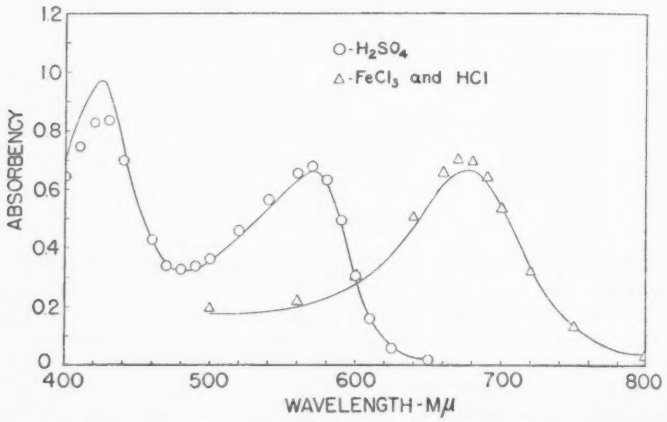

FIGURE 9.—*Spectral absorbency obtained with the carbohydrate concentrate from hide powder, after reaction with orcinol, and with orcinol and ferric chloride at 25° C.*

The ordinates of the smooth curves were calculated to represent a mixture of equal quantities of glucose and galactose.

aldohexoses with orcinol in sulfuric acid at 25° C, giving different ratios of the absorbency in the yellow band to that in the blue band. An attempt was made to represent the absorbencies of all the sugars as the sum of two component absorbencies, which are supposed to arise from the presence of the same two substances in different amounts. At wavelengths greater than 520 mμ, the ratios of the absorbencies of the various sugars are nearly constant, so that these ratios may be taken as the ratios of the amounts of the substance absorbing in the yellow. It was not possible, however, to represent the absorbencies in the green and blue as arising from only two substances.[5] Thus at least three absorption bands are involved in the observed color.

If it is assumed that no substance with more than one absorption band in the visible region is formed in the color reaction, a lower bound for the efficiency of the absorption process may be calculated from the total concentration of sugar and the integral of the absorbency with respect to the frequency. This lower bound in turn permits an estimate to be made of a lower bound for the amount of sugar that is converted to colored substances, as it is impossible for the efficiency to be greater than unity, and it is reasonable to assume that it is not

[5] That is, if the absorbency for the ith sugar is represented as $F_i(\lambda)$, and a_i and b_i are constants characteristic of the ith sugar, no two functions $f_a(\lambda)$ and $f_b(\lambda)$ exist, such that the equations $F_i(\lambda)=a_i f_a(\lambda)+b_i f_b(\lambda)$ are satisfied for all values of i.

greater than 0.6 (for example, the efficiency for methylene blue at pH 3.4 in water is 0.45 [10]). The apparent efficiencies were calculated for galactose with sulfuric acid at 25° C, and for gulose with ferric chloride and hydrochloric acid. The results were 0.4 and 0.2, respectively. Thus the efficiencies of the two absorption processes are at least 0.4 and 0.2, and it may be supposed that at least 0.7 and 0.3 of the respective sugars are converted to colored substances.

IV. SUMMARY

Three colorimetric methods are used to investigate the carbohydrate in collagen from hide, tendon, and bone. The results indicate that the three collagen preparations all contain the same amount of the same kind of carbohydrate. With this evidence in confirmation of results of other comparisons, it may be concluded that the white fibrous connective tissues of the hide, tendon, and bone of the steer are chemically identical. By the use of a fermentation technique, it is demonstrated that the collagen hydrolyzate contains no considerable amount of either free *d*-glucose or free *d*-galactose. The color reactions of a concentrate of the carbohydrate complex are closely similar to those of a mixture of equal quantities of glucose and galactose, which indicates that the carbohydrate either is bound by a difficultly hydrolyzable linkage or is composed of a mixture of *l*-glucose and *l*-galactose. A lower bound for the efficiency of the absorption of light by the colored substances formed from certain sugars was calculated. The result shows that a large fraction of the sugar was converted to the colored substances by the reaction.

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HEATS OF ISOMERIZATION OF THE NINE HEPTANES

By Edward J. R. Prosen and Frederick D. Rossini

ABSTRACT

The heats of isomerization of all of the nine heptanes except 2-methylhexane and 3-methylhexane were determined by measurement of the ratios of their heats of combustion in the liquid state, using the procedure previously described for the hexanes. Values for 2-methylhexane and 3-methylhexane were calculated from the corresponding experimental values for the isomerization of *n*-hexane into 2-methylpentane and 3-methylpentane and of *n*-octane into 2-methylheptane and 3-methylheptane, respectively.

The following values were obtained for the liquid state at 25° C, and were calculated to the gaseous state at 25° C and 0° K:

Isomer	Heat of isomerization, ΔH, for n-C_7H_{16}=i-C_7H_{16}		
	Liquid	Gas	
	25° C	25° C	0° K
	kcal/mole	*kcal/mole*	*kcal/mole*
n-Heptane	0	0	0
2-Methylhexane	−1.30 ±0.25	−1.80 ±0.29	−1.21 ±0.31
3-Methylhexane	−0.72 ±0.25	−1.18 ±0.29	−0.42 ±0.31
3-Ethylpentane	−.14 ±0.23	−0.52 ±0.27	+.48 ±0.30
2,2-Dimethylpentane	−3.42 ±0.28	−4.45 ±0.32	−3.40 ±0.34
2,3-Dimethylpentane	−2.18 ±0.26	−2.80 ±0.30	−1.71 ±0.32
2,4-Dimethylpentane	−2.54 ±0.16	−3.40 ±0.22	−2.32 ±0.25
3,3-Dimethylpentane	−2.44 ±0.15	−3.24 ±0.21	−2.23 ±0.24
2,2,3-Trimethylbutane	−3.00 ±0.22	−4.17 ±0.27	−3.02 ±0.30

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I. INTRODUCTION

In continuation of the program of determining the heats of formation and of isomerization of the paraffin hydrocarbons [1, 2],[1] calorimetric

[1] Figures in brackets indicate the literature references at the end of this paper. References to all the earlier papers are given in [1].

measurements have been made which yield values for the differences in the heats of combustion of all of the nine heptanes, except 2-methylhexane and 3-methylhexane, for the liquid state at 25° C. Values for the latter two, in reference to *n*-heptane, were determined from the corresponding values for the differences in the heats of combustion of *n*-hexane, 2-methylpentane, and 3-methylpentane, the data for which have already been published [2], and of *n*-octane, 2-methylheptane and 3-methylheptane, which have been determined but not yet published [3]. These values for the differences in the heats of combustion, which are also the heats of isomerization in the liquid state at 25° C, have been combined with calculated values for the differences in the heats of vaporization to give values for the heats of isomerization in the gaseous state at 25° C. Combination of these with values for the decrease in heat content of the various isomers in the gaseous state from 25° C to 0° K gives values for the heats of isomerization for the ideal gaseous state at 0° K.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values reported in this paper are based is the International joule. For conversion to the conventional artificial, or defined, calorie, the following relation is used [1]:

4.1833 International joules=1 calorie.

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1941 table of atomic weights [4].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [5].

Definitions of all the symbols used are given in the previous publication [2].

III. METHOD AND APPARATUS

The same method and apparatus were used in the present investigation as in the work on the hexanes [2].

IV. EXPERIMENTAL PROCEDURES

1. CHEMICAL

The description of the heptanes investigated is as follows:

n-Heptane.—Relatively pure *n*-heptane, prepared commercially[3] for use as an automotive antiknock standard, was further purified by distillation in a column having a separating efficiency equivalent to about 100 theoretical plates [6], with subsequent filtration through silica gel [9]. The purified material contained 0.0012 ±0.0002 mole fraction of impurity as determined by A. R. Glasgow, Jr., of the API Research Project 6 at this Bureau, from time-temperature freezing curves [7].

3-Ethylpentane.—This isomer was synthetic material prepared and purified at this Bureau by Brooks, Howard, and Crafton [8], who have described its preparation, purification, and properties. While

[3] Carbide and Carbon Chemicals Corp., New York, N. Y.

these authors did not make a quantitative determination of the amount of impurity in this material, the nature of the distillation and freezing curves indicated it to be one of their purer compounds. Before use in the present investigation, the material was filtered through silica gel [9].

2,2-Dimethylpentane and 3,3-dimethylpentane.—These isomers were obtained by the further purification of material synthesized by Soroos and Willis [11] and kindly made available for this investigation by George Callingaert of the Ethyl Gasoline Corporation, Detroit, Mich. The additional purification consisted in azeotropic distillation with methyl alcohol [10] through a column having a separating efficiency equivalent to about 140 theoretical plates [6], with subsequent filtration through silica gel [9]. The purified materials contained the following amounts of impurity, as determined by A. R. Glasgow, Jr., from time-temperature freezing and melting curves [7]: 2,2-dimethylpentane, 0.0015 ± 0.0005 mole fraction; 3,3-dimethylpentane, 0.0003 ± 0.0002 mole fraction.

2,3-Dimethylpentane and 2,4-dimethylpentane.—These isomers were from synthetic material prepared and purified by the section on Automotive Power Plants at this Bureau [12]. Before use, the hydrocarbons were filtered through silica gel [9]. No quantitative determination was made of the amount of impurity in either of these two compounds. For 2,4-dimethylpentane, the nature of the distillation and freezing curves indicated it to be of a purity comparable to that of the 3-ethylpentane described above [12]. The 2,4-dimethylpentane had a freezing point in air at 1 atm of $-119.86°$ C [12], and the amount of impurity in it was estimated to be 0.006 ± 0.004 mole fraction. For 2,3-dimethylpentane, no freezing curves were obtained, and the nature of the distillation curve indicated it to be of a lesser purity than the 2,4-dimethylpentane [12]. The amount of impurity in the 2,3-dimethylpentane was estimated to be 0.03 ± 0.02 mole fraction.

2, 2, 3-Trimethylbutane.—This isomer was synthetic material kindly placed at our disposal by George Callingaert of the Ethyl Gasoline Corporation, Detroit, Mich. It was further purified by crystallization with centrifuging, with subsequent filtration through silica gel [9]. The purified material contained 0.009 ± 0.002 mole fraction of impurity, as determined by A. R. Glasgow, Jr., from time-temperature freezing curves [7].

It is important to note that the heptanes used were so prepared and purified that the residual impurities must have consisted largely of isomeric heptanes. Further, the impurities would be only those having boiling points near that of the given isomer. The values given in table 1 indicate the olerances with regard to such impurities, and also the actual amounts of impurity. From these data it appears that the amounts of impurity in each of the seven heptanes investigated were not sufficient to affect significantly their heats of combustion.

The procedures for sealing the hydrocarbons in glass ampoules, purifying the oxygen used for combustion, igniting the hydrocarbon, examining the products of combustion, and determining the amount of reaction have been described previously [2].

2. CALORIMETRIC

The calorimetric procedure was the same as that in the work on the hexanes [2].

V. RESULTS

The experimental results of the present investigation are presented in tables, 2, 3, 4, 5, 6, 7, and 8, which give the data yielding values of B in ohms per gram of carbon dioxide, as defined by eq 4 of the previous paper [2], for n-heptane, 3-ethylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethyl pentane, and 2,2,3-trimethylbutane, respectively, in the liquid state at 28° C. The symbols have the same significance as in the previous paper [2]. The value of the heat of isomerization was obtained by means of the relation [2]:

$$(-\Delta U_B)_n-(-\Delta U_B)_i=(-\Delta U_B)_n(1-B_i/B_n).$$

For this calculation the value of $(-\Delta U_B)_n$ was taken as 4,803 kj/mole [13].

TABLE 1.—*Tolerances of the amounts of close-boiling isomeric impurities in the heptanes*

Compound	Possible major impurities	Amount of each such impurity required to change the heat of combustion by 5 parts in 100,000	Amount of impurity in the material used in this work
		Mole fraction	*Mole fraction*
n-Heptane			0.0012 ±0.0002
3-Ethylpentane	3-methylhexane	0.10	•.006 ±0.004
	2-methylhexane	.05	
2, 3-Dimethylpentane	2-methylhexane	.07	•.03 ±0.02
3, 3-Dimethylpentane	2, 3-dimethylpentane	.22	.0003 ±0.0002
2, 2, 3-Trimethylbutane	2, 2-dimethylpentane	.14	.009 ±0.002
	2, 4-dimethylpentane	.13	
2, 4-Dimethylpentane	2, 2-dimethylpentane	.07	•.006 ±0.004
	2, 2, 3-trimethylbutane	.13	
2, 2-Dimethylpentane	2, 4-dimethylpentane	.07	.0015 ±0.0005
	2, 2, 3-trimethylbutane	.14	

• Estimate, not determined quantitatively.

TABLE 2.—*n-Heptane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B•	Deviation from mean
	g	*min*$^{-1}$	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g* CO_2	*Ohms/g* CO_2
1	2.69665	0.001955	0.000742	0.000413	0.305524	0.000423	0.000093	0.1130802	−0.0000051
2	2.71804	.001961	.000709	.000422	.307941	.000415	.000092	.1130829	−.0000024
3	2.33331	.001956	.001875	.000349	.264397	.000417	.000078	.1130689	−.0000164
4	2.20202	.001960	.002310	.000368	.249606	.000415	.000077	.1130946	.0000093
5	2.40038	.001948	.001678	.000342	.272024	.000414	.000043	.1131031	.0000178
6	2.22713	.001954	.002238	.000278	.252448	.000434	.000039	.1131036	.0000183
7	2.37067	.001964	.001771	.000408	.268559	.000404	.000041	.1130639	−.0000214
Mean								0.1130853	
Standard deviation of the mean								±0.0000060	

• Corrected to the standard calorimetric system and to 28.00° C.

TABLE 3.—*3-Ethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min*$^{-1}$	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g* CO_2	*Ohms/g* CO_2
1	2.44412	0.001956	0.001499	0.000638	0.267877	0.000412	0.000081	0.1130525	−0.0000191
2	2.55514	.001951	.001121	.000640	.289438	.000412	.000086	.1130552	−.0000164
3	2.62973	.001960	.000288	.000578	.297910	.000412	.000089	.1130721	.0000005
4	2.30390	.001952	.001916	.000627	.261095	.000417	.000077	.1130805	.0000089
5	2.39864	.001937	.001627	.000558	.271849	.000413	.000082	.1130975	.0000259
Mean								0.1130716	
Standard deviation of the mean								±0.0000083	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 4.—*2,2-Dimethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min*$^{-1}$	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g* CO_2	*Ohms/g* C_3
1	2.59807	0.001962	0.001113	0.000347	0.293569	0.000429	0.000087	0.1127684	0.0000199
2	2.57774	.001957	.001169	.000350	.291268	.000413	.000081	.1127734	.0000249
3	2.61289	.001957	.001039	.000317	.295146	.000415	.000048	.1127523	.0000038
4	2.29817	.001949	.001868	.000363	.259599	.000422	.000041	.1127243	−.0000242
5	2.77610	.001953	.000578	.000344	.313468	.000418	.000048	.1127240	−.0000245
Mean								0.1127485	
Standard deviation of the mean								±0.0000105	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 5.—*2,3-Dimethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min*$^{-1}$	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g* CO_2	*Ohms/g* CO_2
1	2.71689	0.001956	0.000723	0.000381	0.307129	0.000415	0.000092	0.1128330	−0.0000365
2	2.66418	.001957	.000846	.000374	.301333	.000410	.000088	.1128927	.0000232
3	2.80302	.001964	.000368	.000443	.316925	.000407	.000093	.1128642	−.0000053
4	2.20959	.001956	.002290	.000398	.249934	.000411	.000080	.1128553	−.0000142
5	2.16932	.001944	.002401	.000360	.245448	.000425	.000073	.1128792	.0000097
6	2.41740	.001935	.001547	.000277	.273440	.000416	.000042	.1128924	.0000229
Mean								0.1128695	
Standard deviation of the mean								±0.0000095	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 6.—*2,4-Dimethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_i	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min*$^{-1}$	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g* CO_2	*Ohms/g* CO_2
1	2.56395	0.001960	0.001233	0.000326	0.289884	0.000407	0.000091	0.1128400	0.0000046
2	2.41832	.001963	.001654	.000315	.273421	.000409	.000080	.1128303	−.0000051
3	2.54547	.001951	.001234	.000397	.287796	.000415	.000088	.1128366	.0000012
4	2.58308	.001954	.001113	.000368	.292052	.000409	.000086	.1128449	.0000095
5	2.26723	.001955	.002120	.000306	.256334	.000415	.000041	.1128250	−.0000104
Mean								0.1128354	
Standard deviation of the mean								±0.0000035	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 7.—*3,3-Dimethylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_i	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min*$^{-1}$	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g* CO_2	*Ohms/g* CO_2
1	2.82133	0.001954	0.000326	0.000557	0.318930	0.000413	0.000095	0.1128396	−0.0000043
2	2.73915	.001948	.000622	.000578	.309675	.000418	.000092	.1128445	.0000006
3	2.78168	.001956	.000479	.000549	.314480	.000412	.000105	.1128445	.0000006
4	2.76041	.001958	.000552	.000592	.312089	.000414	.000095	.1128505	.0000066
5	2.69239	.001958	.000702	.000438	.304380	.000413	.000089	.1128403	−.0000036
Mean								0.1128439	
Standard deviation of the mean								±0.0000019	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 8.—*2,2,3-Trimethylbutane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_i	Δr_i	Δr_n	B^a	Deviation from mean
	g	*min*$^{-1}$	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms*	*Ohms/g* CO_2	*Ohms/g* CO_2
1	2.26429	0.001947	0.002065	0.000101	0.255903	0.000417	0.000077	0.1128059	0.0000170
2	2.53725	.001948	.001127	.000131	.286617	.000406	.000083	.1127835	−.0000054
3	2.70182	.001945	.000506	.000173	.305223	.000411	.000092	.1127990	.0000101
4	2.55395	.001946	.001131	.000099	.288454	.000408	.000091	.1127628	−.0000261
5	2.39197	.001962	.001677	.000368	.270370	.000414	.000043	.1128087	.0000198
6	2.57436	.001959	.001155	.000362	.290854	.000415	.000044	.1127736	−.0000153
Mean								0.1127889	
Standard deviation of the mean								±0.0000076	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 9.—*Heats of isomerization of the heptanes in the liquid state* [a]

Substance	B at 28.00° C	Ratio of the heats of combustion in the bomb process B_i/B_n at 28° C	Difference in the heats of combustion in the bomb process [b] $(-\Delta U_B)_n-(-\Delta U_B)_i$ at 28° C	Heat of isomerization of the liquid H_i° (liq) $-H_n^\circ$ (liq) at 25° C	
	Ohms/g CO_2		*kj/mole*	*kj/mole*	*kcal/mole*
n-Heptane	0.1130853 ±0.0000120	1.000000	0.00	0.00	0.00
2-Methylhexane					−1.30 ±0.25
3-Methylhexane					−0.72 ±0.25
3-Ethylpentane	.1130716 ±0.0000166	.999879 ±0.000205	0.58 ±0.98	−0.57 ±0.98	−.14 ±0.23
2, 2-Dimethylpentane	.1127485 ±0.0000210	.997022 ±0.000242	14.30 ±1.16	−14.29 ±1.16	−3.42 ±0.28
2, 3-Dimethylpentane	.1128695 ±0.0000190	.998092 ±0.000225	9.16 ±1.08	−9.14 ±1.08	−2.18 ±0.26
2, 4-Dimethylpentane	.1128354 ±0.0000070	.997790 ±0.000139	10.61 ±0.67	−10.61 ±0.67	−2.54 ±0.16
3, 3-Dimethylpentane	.1128439 ±0.0000038	.997865 ±0.000126	10.25 ±0.61	−10.22 ±0.61	−2.44 ±0.15
2, 2, 3-Trimethylbutane	.1127889 ±0.0000152	.997379 ±0.000194	12.59 ±0.93	−12.56 ±0.93	−3.00 ±0.22

[a] All the uncertainties assigned to the experimental quantities in this table are equal to twice the standard deviation [5]. The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may conservatively be taken, on the average, as ±0.25 kcal/mole.

[b] Obtained by subtracting the value in column 3 from unity and multiplying with the factor 4,803 kj/mole (see section VI).

TABLE 10.—*Heats of isomerization of the nine heptanes in the gaseous state* [a]

Substance	Heat of isomerization of the liquid H_i° (liq) $-H_n^\circ$ (liq) at 25° C		Difference in the heats of vaporization $(\Delta H^\circ_{vap})_n-(\Delta H^\circ_{vap})_i$ at 25° C	Heat of isomerization of the gas H_i° (g) $-H_n^\circ$ (g) at 25° C	$(H^\circ_{298}-H^\circ_0)_n-(H^\circ_{298}-H^\circ_0)_i$	Heat of isomerization of the gas H_i° (g) $-H_n^\circ$ (g) at 0° K
	kj/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*	*kcal/mole*	*kcal/mole*
n-Heptane	0	0	0	0	0	0
2-Methylhexane		−1.30 ±0.25	0.50 ±0.15	−1.80 ±0.29	0.59 ±0.12	−1.21 ±0.31
3-Methylhexane		−0.72 ±0.25	.46 ±0.15	−1.18 ±0.29	.76 ±0.12	−.42 ±0.31
3-Ethylpentane	−0.57 ±0.98	−.14 ±0.23	.38 ±0.15	−.52 ±0.27	1.00 ±0.12	+.48 ±0.30
2, 2-Dimethylpentane	−14.29 ±1.16	−3.42 ±0.28	1.03 ±0.15	−4.45 ±0.32	1.05 ±0.12	−3.40 ±0.34
2, 3-Dimethylpentane	−9.14 ±1.08	−2.18 ±0.26	0.62 ±0.15	−2.80 ±0.30	1.09 ±0.12	−1.71 ±0.32
2, 4-Dimethylpentane	−10.61 ±0.67	−2.54 ±0.16	.86 ±0.15	−3.40 ±0.22	1.08 ±0.12	−2.32 ±0.25
3, 3-Dimethylpentane	−10.22 ±0.61	−2.44 ±0.15	.80 ±0.15	−3.24 ±0.21	1.01 ±0.12	−2.23 ±0.24
2, 2, 3-Trimethylbutane	−12.56 ±0.93	−3.00 ±0.22	1.17 ±0.15	−4.17 ±0.27	1.15 ±0.12	−3.02 ±0.30

[a] The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may be taken as ±0.25 kcal/mole for the liquid at 25° C, ±0.29 kcal/mole for the gas at 25°C, and ±0.31 kcal/mole for the gas at 0°K.

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TABLE 11.—*Comparison of the three sets of data on the heats of isomerization of the nine heptanes in the liquid state at 25° C*

Isomer	H_i° (liq) − H_n° (liq) at 25° C		
	Present work	Jessup [16]*	Davies and Gilbert [17]*
	kcal/mole	*kcal/mole*	*kcal/mole*
n-Heptane	0	0	0
2-Methylhexane	−1.30 ±0.25	−1.4 ±1.0	−1.25 ±0.40
3-Methylhexane	−0.72 ±0.25	−0.8 ±1.0	−0.52 ±0.50
3-Ethylpentane	−.14 ±0.23	+.1 ±1.0	−.19 ±0.40
2, 2-Dimethylpentane	−3.42 ±0.28	−3.6 ±1.0	−3.91 ±0.40
2, 3-Dimethylpentane	−2.18 ±0.26	−1.2 ±1.0	−1.70 ±0.40
2, 4-Dimethylpentane	−2.54 ±0.16	−1.2 ±1.0	−2.99 ±0.40
3, 3-Dimethylpentane	−2.44 ±0.15	−2.2 ±1.0	−3.03 ±0.50
2, 2, 3-Trimethylbutane	−3.00 ±0.22	−2.5 ±1.0	−2.80 ±0.30

* See text for discussion of these values.

In table 9 are given, for the seven isomeric heptanes investigated, values for the following: the constant B in ohms per gram of carbon dioxide, as given in tables 2 to 8, inclusive; the ratio of the heat evolved, per mole of hydrocarbon, in the bomb process at 28° C for each isomer to that for *n*-heptane; the difference, between *n*-heptane and each isomer, in the heat of combustion in the bomb process at 28° C; and the heat of isomerization, for the liquid state at 25° C and 1 atm, of *n*-heptane into each isomer. Values for the last-named property are also given in the last column of table 9 for 2-methylhexane and 3-methylhexane. These were obtained in the following way:

In the previous paper [2], the heat of isomerization of *n*-hexane into 2-methylpentane and 3-methylpentane, respectively, for the liquid state at 25° C and 1 atm, were determined to be −1.30 ±0.21 and −0.76 ±0.19 kcal/mole. Unpublished data obtained by the authors yield for the heats of isomerization of *n*-octane into 2-methylheptane and 3-methylheptane, respectively, for the liquid state at 25° C and 1 atm, the values −1.50 ±0.30 and −0.63 ±0.30 kcal/mole. The values for the heat of isomerization of *n*-heptane into 2-methylhexane and 3-methylhexane, respectively, for the liquid state at 25° C and 1 atm, were taken as the weighted means of the corresponding values for the analogous hexanes and octanes.

In table 10 are given values for the following: the heat of isomerization, for the liquid state at 25° C, of *n*-heptane into each isomer, as given in table 9; the difference, between *n*-heptane and each isomer, in the heat of vaporization at 25° C for the gas in the ideal state [14]; the heat of isomerization, for the ideal gaseous state, of *n*-heptane into each isomer at 25° C; the difference, between *n*-heptane and each isomer, in the value of $H_{298}^\circ - H_0^\circ$, the heat content at 298° K referred to the absolute zero, for the ideal gaseous state [18]; and, finally, the heat of isomerization, for ideal gaseous state, of *n*-heptane into each isomer at 0° K.

VI. DATA OF PREVIOUS INVESTIGATIONS

Prior to 1941 the only published works on the determination of the heats of combustion for any of the heptanes were those of Louguinine [15] and Jessup [13], each of whom measured *n*-heptane only. There

are available to the authors, however, two sets of data involving the nine isomeric heptanes, which may be compared with the results of the present investigation.

The first set of such values are from some unpublished data obtained by Jessup [16] at this Bureau in 1927, in an investigation in which circumstances made it possible to perform only two combustion experiments on each of eight isomers and three on the remaining one. In a number of these experiments, a significant amount of carbon remained unburned. Because of the then unavoidable limitations placed upon these experiments of Jessup, the values of the heats of isomerization deduced from the unpublished data that he has kindly placed at our disposal are arbitrarily assigned an uncertainty of ± 1.0 kcal/mole. These values are shown in table 11 in comparison with the present values.

The second set of data available for comparison are those recently obtained by Davies and Gilbert [17]. In their investigation, the purity of the isomers was not determined quantitatively, and the amount of reaction was in each case computed from the mass of liquid placed in the bomb. The values of the heats of isomerization obtained from their data are shown in table 11 in comparison with the values from the present investigation. The uncertainties are those assigned by Gilbert in a private communication to the authors.

All of the values given in table 11 are substantially in accord, within their assigned limits of uncertainty.

VII. DISCUSSION

As has been previously pointed out, values of the heats of isomerization of the heptanes, along with those of the other paraffin hydrocarbons, are needed in studying the influence of structure upon the energy content of the molecule and in calculating, in combination with entropies or the free energy functions, values of the free energies of isomerization.

With regard to the correlation of the energy content with structure, it is planned to report the results of such a study after the heats of isomerization of the 18 octanes, and perhaps 1 or 2 selected nonanes, have been determined. For the present, it may be sufficient to point out that the data reported here on the heats of isomerization of the heptanes follow the generalization already made by one of the authors [1] concerning the change with structure of the energy content of isomeric hydrocarbons. This generalization may be stated as follows: With regard to energy content, the stability of the molecule increases with increase in the compactness of the carbon skeleton, up to the point where too close proximity of the hydrogen atoms on different carbon atoms produces a decrease in the stability of the molecule. The most stable isomer, with regard to energy content, appears to be that one which has a maximum of compactness and at the same time has the hydrogen atoms so disposed as to interfere little with one another. This is illustrated by the fact that the 2,2-dimethyl isomer is uniformly the most stable at 0° K, and that the 3-methyl and 3-ethyl isomers are the least stable of the branched chain isomers. It may also be noted that, at 0° K, 2,2-dimethylpentane appears to be slightly more stable than the more highly branched isomer, 2,2,3-trimethylbutane, and definitely more stable than 3,3-dimethylpentane.

Substitution on the 3- position tends to produce instability because of interference among the hydrogen atoms.

Research Paper RP1440 [19] illustrates the use of the data on heats of isomerization reported here in calculating free energies of isomerization.

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FREE ENERGIES AND EQUILIBRIA OF ISOMERIZATION OF THE BUTANES, PENTANES, HEXANES, AND HEPTANES [1]

By Frederick D. Rossini, Edward J. R. Prosen, and Kenneth S. Pitzer [2]

ABSTRACT

There are presented in tabular and graphical form, for the two butanes, the three pentanes, the five hexanes, and the nine heptanes, all in the ideal gaseous state, for the range 298° to 1,000° K, values of the following thermodynamic properties: (a) the standard free energy of isomerization divided by the absolute temperature, $\Delta F^\circ/T$; and (b) the relative amounts of the several isomers present when at equilibrium with each other. Comparison is made of these calculated values of the equilibrium concentrations with the directly measured values reported by other investigators for equilibria involving (a) the two butanes, (b) two pentanes, and (c) four hexanes.

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I. INTRODUCTION

In this paper there are reported values of the standard free energies of isomerization, and the corresponding equilibrium concentrations, for the two butanes, the three pentanes, the five hexanes, and the nine heptanes, all in the ideal gaseous state, for the range 298° to 1,000° K. These values have been calculated in the following way:

There are given in papers already published, values of the heat of isomerization at 0° K, ΔH_0°, for the normal paraffin to the branched-chain isomer [10, 11, 9], and values of the free-energy function, $(F^\circ - H_0^\circ)/T$, for each isomer [8].[3] For the isomerization of the normal paraffin to the isoparaffin (normal and iso being indicated by the italic letters n and i, respectively),

$$n\text{-}C_aH_b\ (\text{gas}) = i\text{-}C_aH_b\ (\text{gas}), \tag{1}$$

ΔF° is the standard free-energy change at a given temperature, with each component in its ideal standard state of unit fugacity, and

$$\Delta\left(\frac{F^\circ - H_0^\circ}{T}\right) = \left(\frac{F^\circ - H_0^\circ}{T}\right)_i - \left(\frac{F^\circ - H_0^\circ}{T}\right)_n. \tag{2}$$

[1] Presented before the Division of Petroleum Chemistry of the American Chemical Society at Atlantic City, N. J., September 11, 1941.

[2] Professor of Chemistry, University of California, Berkeley, Calif.

[3] Figures in brackets indicate the literature references at the end of this paper.

But

$$\Delta\left(\frac{F^\circ - H_0^\circ}{T}\right) = \frac{\Delta F^\circ}{T} - \frac{\Delta H_0^\circ}{T}, \tag{3}$$

and

$$\frac{\Delta F^\circ}{T} = -R\ln K, \tag{4}$$

where K is the equilibrium constant, as defined by Lewis and Randall [4]. Then

$$\frac{\Delta F^\circ}{T} = -R\ln K = \frac{\Delta H_0^\circ}{T} + \Delta\left(\frac{F^\circ - H_0^\circ}{T}\right). \tag{5}$$

For the isomerization reaction as given by eq 1,

$$K = f_i/f_n, \tag{6}$$

and, for low pressures,

$$K = p_i/p_n, \tag{7}$$

where f represents the fugacity (see [4]) and p the partial pressure.

II. RESULTS IN TABULAR AND GRAPHICAL FORM

The thermodynamic quantities calculated in this way from the data referred to are given in table 1. The first two columns give the temperature in centigrade and Kelvin degrees, respectively, with the former rounded off in reference to the latter, the difference being not at all significant here. The succeeding columns give for each isomer of the butanes, pentanes, hexanes, and heptanes, respectively, values of the following thermodynamic properties: $\Delta F^\circ/T$, which is the standard free-energy change divided by the absolute temperature, for the reaction of isomerization in the gas phase, as expressed by eq 1; K, which is the equilibrium constant, defined by eq 4 and 6, for the reaction expressed by eq 1; and N, which is the mole fraction of the given isomer present when at equilibrium with all of its other isomers. Strictly, the value of N so calculated is applicable only in the range from zero pressure up to that pressure at which the ratio of fugacity to pressure is still not significantly different for the several isomers. Within this range of pressure, the value of K in table 1 gives directly the ratio of the amount of the given isomer to the amount of the normal isomer in equilibrium with it in the gas phase. For any two other isomers, the ratio of the corresponding values of K in table 1 gives the ratio of the amounts of those two isomers present when at equilibrium in the gas phase with one another.

The limits of uncertainty of the values of $\Delta F^\circ/T$ given in table 1 are estimated to be as follows, for the range 298° to 1,000° K: For the butanes, ±0.75 cal/deg mole; for the pentanes, ±1.0 cal/deg mole; for the hexanes, ±1.0 cal/deg mole; and for the heptanes, ±1.3 cal/deg mole. This same uncertainty applies to the value of $\Delta F^\circ/T$ for the isomerization of any one of the isomers into any other one. From these values, one may easily derive the corresponding uncertainties in the values of the equilibrium constants and the equilibrium concentrations, as illustrated in figures 9 and 11. For the purpose of retaining the significance of their change with temperature, the values in table 1 are written with more figures than the foregoing uncertainties would normally warrant.

Temperature		BUTANES						PENTANES									HEXANES											
		n-butane			isobutane			n-pentane			2-methylbutane			2,2-dimethylpropane			n-hexane			2-methylpentane			3-methylpentane			2,2-dimethylbutane			2,3-dimethylbutane		
Centigrade t	Kelvin T	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N
°C	°K	cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole		
(25)	298	0	1	0.28	-1.86	2.55	0.72	0	1	0.03	-5.28	14.3	0.44	-5.65	17.1	0.53	0	1	0.013	-3.33	5.34	0.071	-1.25	1.88	0.025	-3.22	4.24	0.084	-2.78	4.05	0.054
(127)	400	0	1	.44	-0.47	1.27	.56	0	1	.11	-3.64	6.23	.65	-1.65	2.30	.24	0	1	.061	-1.98	2.71	.16	-0.43	1.24	.075	-1.58	1.90	.161	-0.81	1.51	.092
(227)	500	0	1	.54	0.35	0.84	.46	0	1	.18	-2.68	3.86	.69	0.59	0.74	.13	0	1	.13	-1.25	1.83	.24	0.09	0.96	.12	-2.37	3.30	.41	0.35	0.84	.105
(327)	600	0	1	.60	0.83	.66	.40	0	1	.24	-2.11	2.89	.47	1.98	.37	.087	0	1	.19	-0.74	1.45	.27	0.39	.92	.15	-0.91	1.58	.29	1.14	.56	.104
(527)	800	0	1	.68	1.44	.48	.32	0	1	.32	-1.38	2.00	.63	3.75	.15	.049	0	1	.26	-0.15	1.08	.28	0.72	.70	.18	0.75	0.69	.18	1.99	.37	.096
(727)	1000	0	1	.72	1.84	.39	.28	0	1	.37	-0.92	1.59	.59	4.78	.09	.034	0	1	.31	0.24	0.89	.27	0.86	.65	.20	1.68	0.43	.13	2.49	.29	.088

Temperature		HEPTANES																														
		n-heptane			2-methylhexane			3-methylhexane (racemic mixture)			3-ethylpentane			2,2-dimethylpentane			2,3-dimethylpentane (racemic mixture)			2,4-dimethylpentane			3,3-dimethylpentane			2,2,3-trimethylbutane					
Centigrade t	Kelvin T	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N	$\Delta F^\circ/T$	K	N			
°C	°K	cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole			cal/deg mole					
(25)	298	0	1	0.009	-4.01	7.52	0.068	-3.62	6.18	0.056	1.43	0.49	0.004	-6.99	33.7	0.30	-6.75	29.9	0.27	-4.57	9.98	0.090	-4.80	11.2	0.100	-4.85	11.5	0.103			
(127)	400	0	1	.032	-2.59	3.68	.12	-2.69	3.87	.13	1.81	.40	.013	-3.09	4.73	.15	-4.49	9.57	.31	-1.79	2.46	.079	-2.29	3.16	.102	-1.47	2.09	.068			
(227)	500	0	1	.062	-1.74	2.40	.15	-2.14	2.94	.18	2.22	.33	.020	-0.84	1.53	.10	-3.08	4.71	.29	-0.18	1.09	.068	-0.62	1.37	.085	0.60	0.74	.046			
(327)	600	0	1	.092	-1.13	1.77	.16	-1.70	2.36	.22	2.47	.29	.027	0.60	0.74	.068	-2.10	2.88	.27	1.00	0.60	.056	0.44	0.80	.074	1.92	.38	.035			
(527)	800	0	1	.14	-0.42	1.24	.17	-1.22	1.85	.26	2.78	.25	.035	2.33	.31	.044	-0.87	1.55	.22	2.38	.30	.043	1.68	.43	.061	3.49	.17	.024			
(727)	1000	0	1	.17	-0.12	1.06	.18	-1.02	1.67	.29	2.96	.23	.039	3.28	.19	.033	-0.14	1.07	.18	3.06	.21	.037	2.34	.31	.053	4.35	.11	.019			

TABLE 1.—*Summary of values of the free energies, equilibrium constants, and equilibrium concentrations, for the isomerization of the butanes, pentanes, hexanes, and heptanes, in the ideal gaseous state, from 298° to 1,000°K.*•

• The estimated uncertainties, expressed for $\Delta F^\circ/T$, from 298° to 1,000° K, are as follows, in cal/deg mole: butanes, ±0.75; pentanes, ±1.00; hexanes, ±1.00; heptanes, ±1.30.

In figures 1, 2, 3, and 4 are plotted, as a function of the temperature, the values of $\Delta F°/T$ given in table 1 for the 19 hydrocarbons.

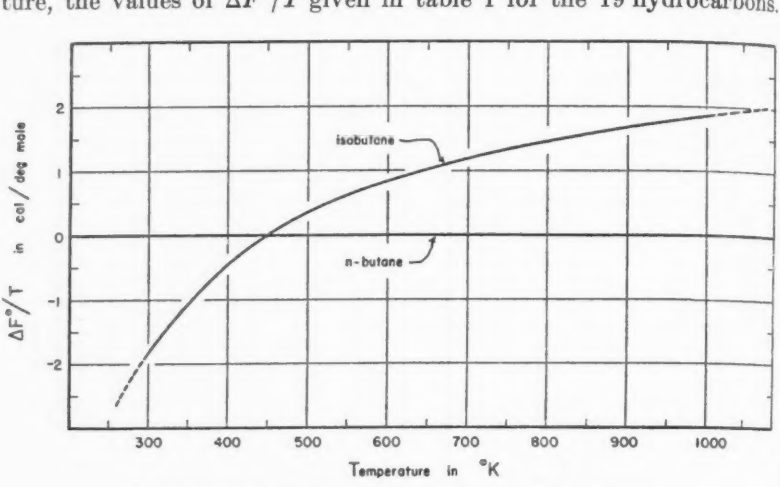

FIGURE 1.—*Free energy of isomerization of the butanes.*

The scale of ordinates gives the value of $\Delta F°/T$, in cal/deg mole, for the isomerization, $n-C_4H_{10}$ (gas) $=i-C_4H_{10}$ (gas). The scale of abscissas gives the temperature in degrees Kelvin.

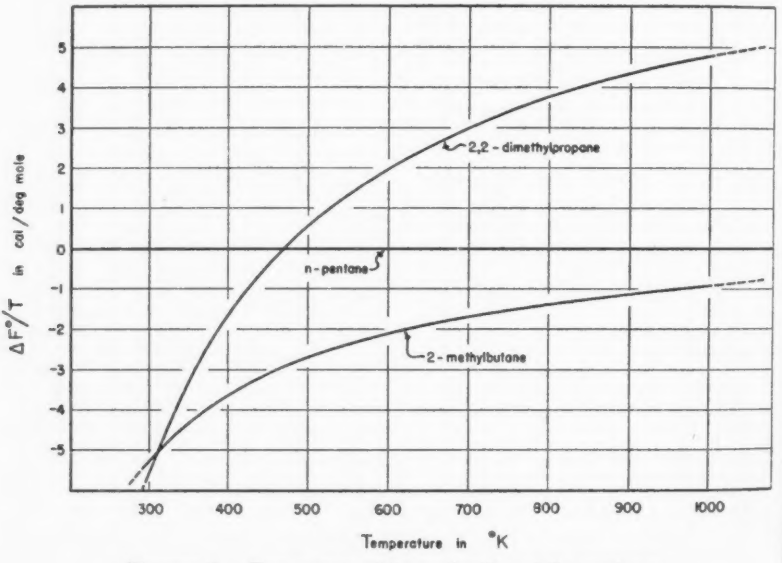

FIGURE 2.—*Free energy of isomerization of the pentanes.*

The scale of ordinates gives the value of $\Delta F°/T$, in cal/deg mole, for the isomerization, $n-C_5H_{12}$ (gas)$=i-C_5H_{12}$ (gas). The scale of abscissas gives the temperature in degrees Kelvin.

From these charts one may see at a glance, for any temperature in the given range and within the limits of uncertainty of the present calculations, which of the isomers is thermodynamically the most

stable (lowest value of $\Delta F°/T$), which is the least stable (highest value of $\Delta F°/T$), and the order of stability of the other isomers. From the preceding discussion regarding uncertainties, it follows that those isomers having at some given temperature values of $\Delta F°/T$ that differ by less than the uncertainty are ones for which the exact order of stability cannot be stated, since the values overlap. In such cases, the amounts present at equilibrium will be equal within the given limits.

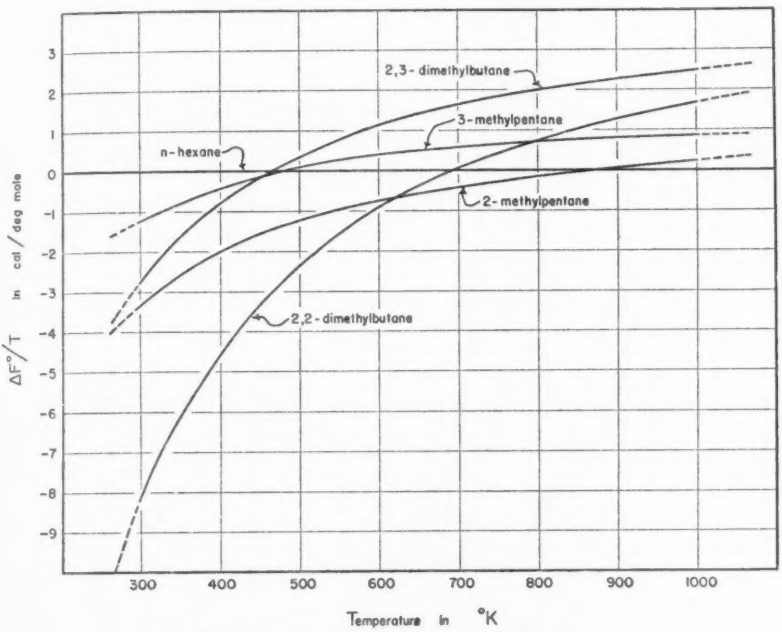

FIGURE 3.—*Free energy of isomerization of the hexanes.*

The scale of ordinates gives the value of $\Delta F°/T$, in cal/deg mole, for the isomerization, $n-C_6H_{14}$ (gas) $= i-C_6H_{14}$ (gas). The scale of abscissas gives the temperature in degrees Kelvin.

In figures 5, 6, 7, and 8 are plotted, as a function of the temperature, for the butanes, pentanes, hexanes, and heptanes, respectively, the amounts, in mole fraction, of each of the isomers present when at equilibrium with all its other isomers in the gas phase, as given in table 1. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures. For example, figure 8 shows how, within the limits of uncertainty previously given, 1 mole of C_7H_{16} molecules distribute themselves among the nine isomeric forms of heptane at thermodynamic equilibrium in the gas phase from 260° to 1060° K, for those pressures where the ratio of fugacity to pressure is substantially the same for the given isomers.

III. COMPARISON WITH DIRECT MEASUREMENTS OF EQUILIBRIA

In figure 9 are compared the available data on the direct determination of the concentrations of *n*-butane and isobutane present

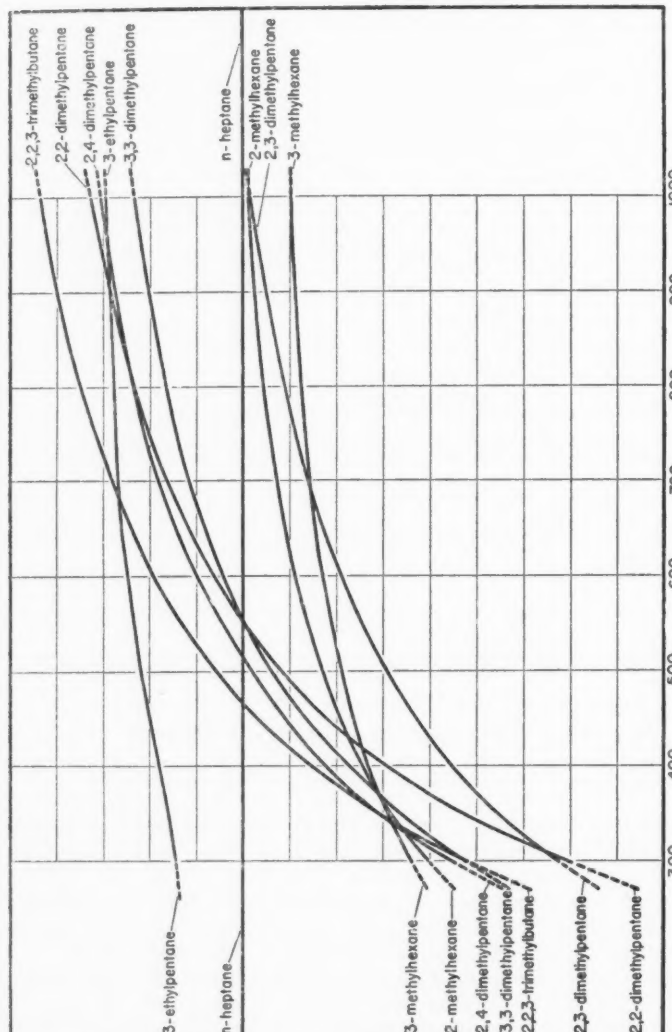

FIGURE 4.—*Free energy of isomerization of the heptanes.*

The scale of ordinates gives the value of $\Delta F^\circ/T$, in cal/deg mole, for the isomerization, n-C_7H_{16} (gas) $\rightleftharpoons$ i-C_7H_{16} (gas). The scale of abscissas gives the temperature in degrees Kelvin. The values given for 3-methylhexane and 2, 3-dimethylpentane are for the racemic mixtures of the optical isomers.

when at equilibrium with one another, as reported by De Simo, McMillan, and Cheney [3], Moldavskii and Nizovkina [5], Montgomery, McAteer, Franke, and Horne [6, 7], and Schuit, Hoog, and Verheus [13], with the values for the same quantities as derived

from table 1. In those several cases where the direct determination of the equilibrium concentrations was made for the liquid phase,

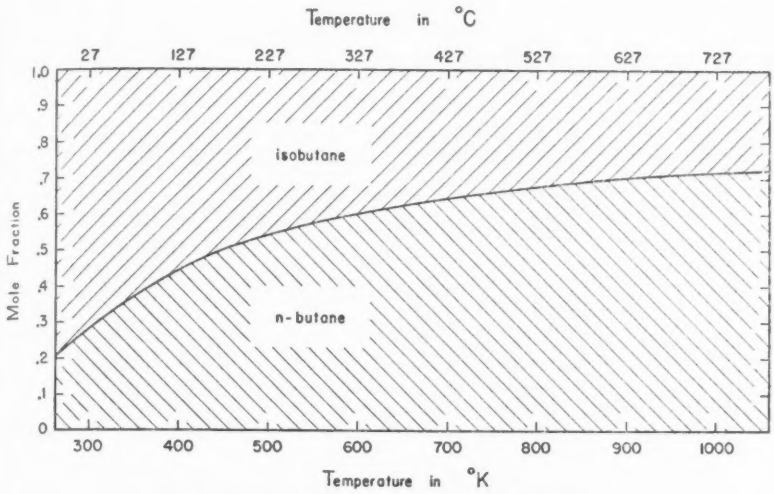

FIGURE 5.—*Equilibrium concentrations of the butanes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

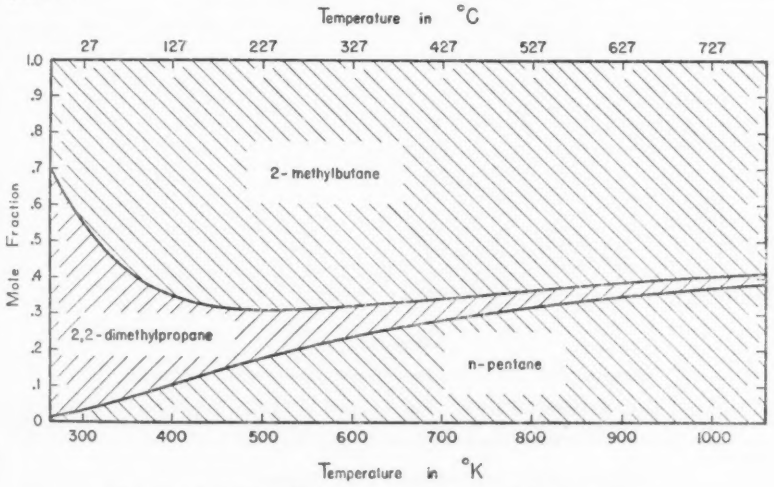

FIGURE 6.—*Equilibrium concentrations of the pentanes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

the observed values were corrected to the gas phase. The solid line in figure 9 represents the amount of *n*-butane in an equilibrium mixture of the two butanes, as derived from the values in table 1. The

broken lines parallel to the solid line indicate the estimated uncertainty in the values derived from table 1. Likewise, the vertical arrows placed on the values of the direct determinations of the equilibrium concentrations represent estimated uncertainties as placed by the present authors. Where the standard deviation of the mean of the observations has been given, this has been multiplied by 2

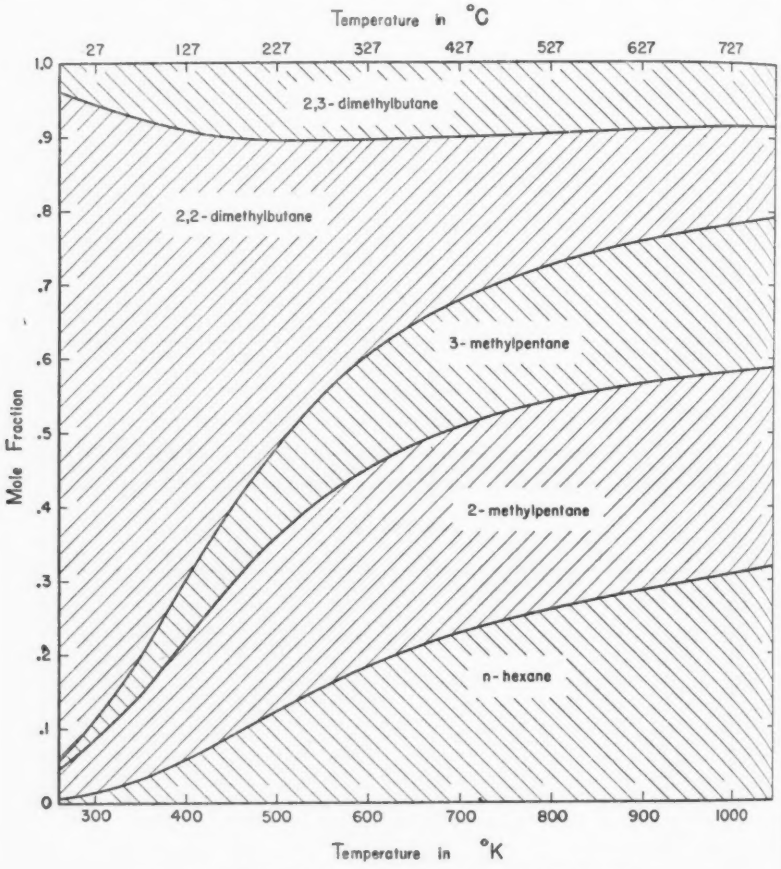

FIGURE 7.—*Equilibrium concentrations of the hexanes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

to yield the estimated uncertainty [12]. It may be seen from figure 9 that the direct determinations of the equilibrium concentrations are almost, but not quite, in accord with the values derived from table 1, within the respective limits of uncertainty.

The values of free energy and equilibrium concentrations given in table 1 are uniformly (see introduction) based upon (I) a combination of (a) values of heats of isomerization determined calorimetrically with (b) values of the free-energy function determined from statistical

calculations and "third-law" entropies. A second set of values may be calculated (II) from a combination of (a) values of the equilibrium concentrations determined experimentally at or near a given selected

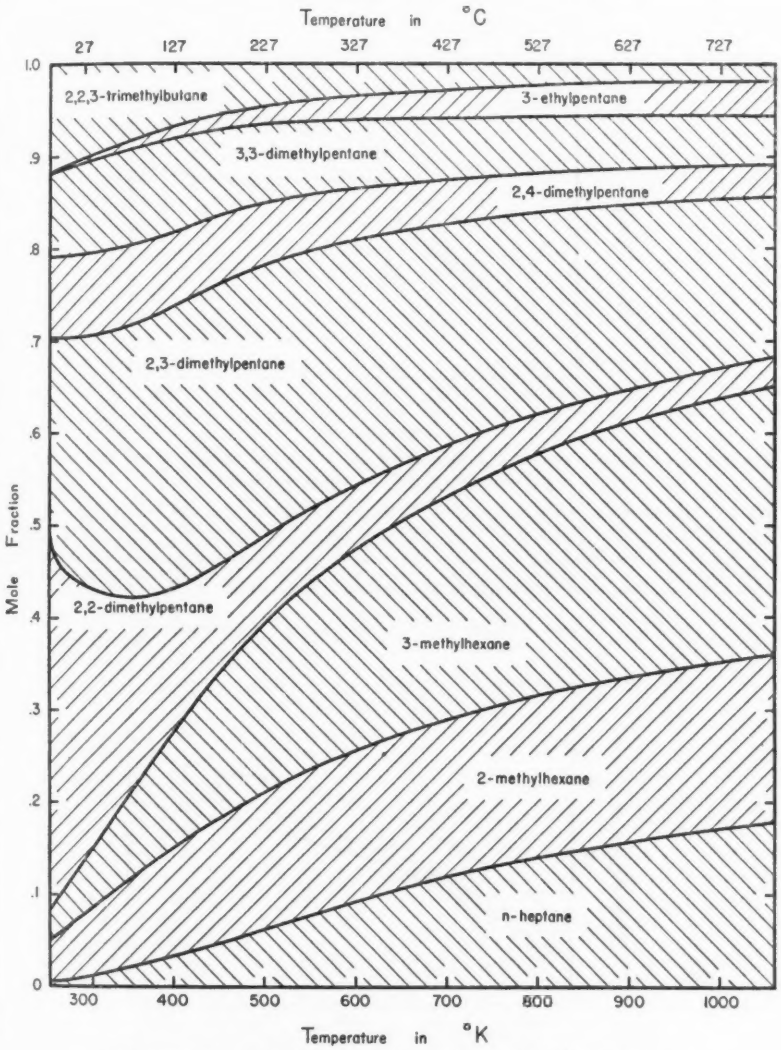

FIGURE 8.—*Equilibrium concentrations of the heptanes.*

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase. The values for 3-methylhexane and 2, 3-dimethylpentane are for the racemic mixture of the optical isomers.

temperature with (b) values of the free-energy function determined from statistical calculations and "third-law" entropies. A third set of values may be calculated (III) from a combination of (a) values of heats of isomerization determined calorimetrically with (b) values of

the equilibrium concentrations determined experimentally at or near a given temperature, together with values of the heat content as a function of the temperature.

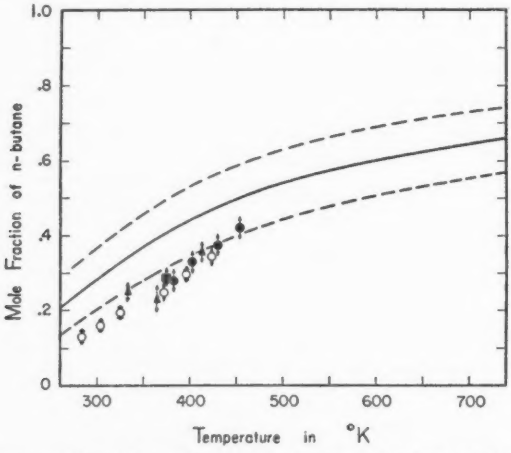

FIGURE 9.—*Comparison of the calculated and observed values of the concentrations for the equilibrium, n-butane (gas) = isobutane (gas).*

The scale of ordinates gives the mole fraction of *n*-butane (gas) at equilibrium with isobutane (gas). The scale of abscissas gives the temperature in degrees Kelvin. The solid line represents the values derived from those in table 1, and the broken lines represent the estimated limits of uncertainty. The points, with vertical arrows indicating the estimated uncertainty, represent observed values from the following investigations: ○, Montgomery, McAteer, Franke, and Thorne [6, 7]; ●, Moldavskii and Nizovkina [5]; ▲, Schuit, Hoog, and Verheus [13]; ■, De Simo, McMillan, and Cheney [3].

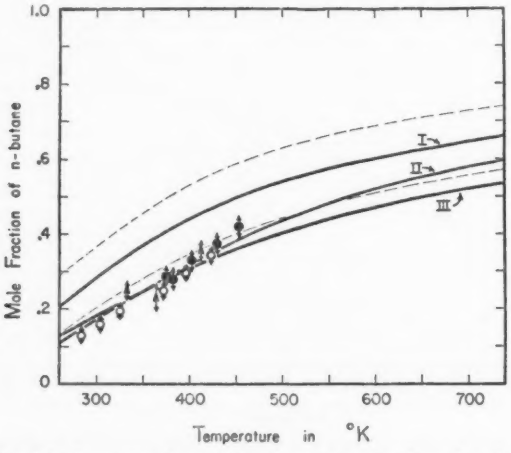

FIGURE 10.—*Graphical comparsion of the three sets of values for the isomerization of the butanes.*

The scale of ordinates gives the mole fraction of *n*-butane (gas) at equilibrium with isobutane (gas.) The scale of abscissas gives the temperature in degrees Kelvin. See text and table 2 for explanation.

Only for the butanes are sufficiently precise data from all three sources available, and in table 2 are presented the three sets of values so calculated for the butanes. Figure 10 shows the three sets of

values of the equilibrium concentrations, together with the experimentally determined values as given in figure 9. As in figure 9, the dashed lines in figure 10 represent the limits of uncertainty of the values represented by curve I. The experimentally observed values of the equilibrium concentrations are obviously in best accord with curves II and III, since they were used to establish the location of these curves. The three sets of values are almost, but not quite, in accord within their respective limits of uncertainty. New and more accurate determinations of the heat of isomerization, or of the entropy of isomerization, or of the actual equilibrium concentrations, will make possible the selection of a final "best" set of values for the isomerization of the butanes.

TABLE 2.—*Comparison of three sets of values for the isomerization of n-butane into isobutane:* $n-C_4H_{10}$ (gas) $= i-C_4H_{10}$ (gas)

[See text and figure 10 for explanation.]

Temperature		I			II			III		
		$\Delta F°/T$	K	N	$\Delta F°/T$	K	N	$\Delta F°/T$	K	N
°C	°K	cal/deg mole			cal/deg mole			cal/deg mole		
25	298	−1.86	2.55	0.72	−3.20	5.0	0.83	−3.00	4.5	0.82
127	400	−0.47	1.27	.56	−1.47	2.10	.68	−1.60	2.25	.69
227	500	.35	0.84	.46	−0.45	1.25	.56	−0.79	1.49	.60
327	600	.83	.66	.40	.17	0.92	.48	−.25	1.13	.53
527	800	1.44	.48	.32	.94	.62	.38	.43	0.80	.44
727	1,000	1.86	.39	.28	1.46	.48	.32	.83	.66	.40

In figure 11 are compared the available data on the direct determination of the concentrations of *n*-pentane and 2-methylbutane present in an equilibrium mixture of the two, as reported by Montgomery,

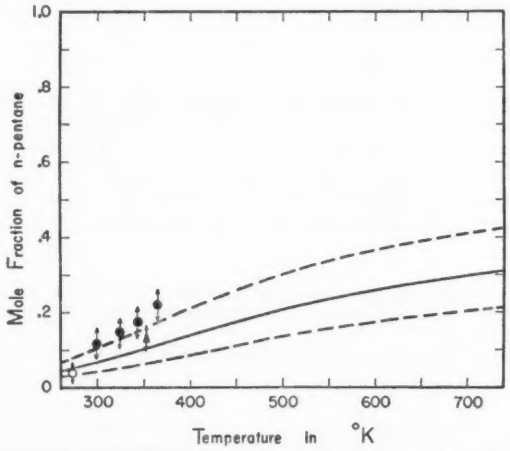

FIGURE 11.—*Comparison of the calculated and observed values of the concentrations for the equilibrium, n-pentane (gas) = 2-methylbutane (gas).*

The scale of ordinates gives the mole fraction on *n*-pentane (gas) at equilibrium with 2-methylbutane (gas in a mixture of the two. The scale of abscissas gives the temperature in degrees Kelvin. The solid line represents values derived from those in table 1, and the broken lines represent the estimated limits of uncertainty. The points, with vertical arrows indicating the estimated uncertainty, represent observed values from the following investigations:
○, Montgomery, McAteer, and Franke [6]; ●, Moldavskii and Nizovkina [15]; ▲, Schuit, Hoog, and Verheus [13].

McAteer, and Franke [6], Schuit, Hoog, and Verheus [13], and Moldavskii and Mzovkina [15], with the values for the same quantities as derived from table 1. The direct observations were made on the liquid phase and have been appropriately corrected to the gas phase. The solid line, the broken lines, and the vertical arrows have the same significance as those in figure 9. Within their respective limits of uncertainty, the directly measured values of the equilibrium concentrations are in accord with the values derived from table 1.

Some data have been reported by Schuit, Hoog, and Verheus [13] on the equilibrium concentrations of four of the five isomers of hexane in the liquid state at 80° C. From the values given in table 1 and plotted in figure 3, the equilibrium concentrations for the gaseous state at 80° C may be calculated. These values may be converted to the liquid state, utilizing values of the ratios of the vapor pressures of the pure components at this temperature and assuming that the partial pressure of a given component in the liquid mixture is equal to its mole fraction times its vapor pressure in the pure state. The results of a comparison of the calculated and observed concentrations are shown in table 3. Within the respective limits of uncertainty, the observed and calculated values are in accord.

TABLE 3.—*Comparison of the calculated and observed concentrations for the equilibrium involving n-hexane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane, in the liquid state at 80° C*

Isomer	Mole fraction		
	Calculated		Observed [13]
	Gas	Liquid	Liquid
n-Hexane	0.12	0.15	0.13 ±0.10
2-Methylpentane	.43	.42	.70 ±0.10
3-Methylpentane	.18	.19	0.61
2,3-Dimethylbutane	.27	.24	.18 ±0.06

Direct experimental measurements recently have been made by Montgomery and coworkers [14] on the equilibrium between the two methylpentanes in the liquid state at 25° C. The results of a comparison of the calculated and observed values of the equilibrium constant for this reaction are shown in table 4. Within the assigned limits of uncertainty, the observed and calculated values are well in accord.

TABLE 4.—*Comparison of the calculated and observed values of the equilibrium constant for the equilibrium between 2-methylpentane and 3-methylpentane in the liquid state at 25° C*

Equilibrium	Equilibrium constant		
	Calculated *		Observed [14]
	Gas	Liquid	Liquid
3-Methylpentane=2-methylpentane	(4.71) 2.84 (1.72)	(4.29) 2.59 (1.57)	1.96 ±0.70

* The values in parentheses above and below the calculated values indicate, respectively, the estimated upper and lower limits of uncertainty.

IV. CONCLUSION

On the basis of the present data, the following general conclusions may be made with regard to the butanes, pentanes, hexanes, and heptanes, in the gaseous state:

(a) At 25° C, the normal isomer is thermodynamically the least stable in each case, with the exception that 3-ethylpentane is less stable than *n*-heptane. Relative to the other isomers, the normal isomer increases in stability with increase in temperature, and at 1,000° K is among the most stable of the isomers.

(b) At 25° C, the 2,2-dimethyl isomer is in each case the most stable, but it rapidly becomes less stable with increasing temperature and at 1,000° K is among the least stable of the isomers.

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WASHINGTON, October 17, 1941.

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RESEARCH PAPER RP1441

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FLUIDITY OF TRITON F AND XANTHATE SOLUTIONS AS A MEASURE OF CELLULOSE DEGRADATION

By Ralph T. Mease and Leland F. Gleysteen[1]

ABSTRACT

Dimethyldibenzylammonium hydroxide (Triton F) and sodium hydroxide solutions containing carbon disulfide were compared with cuprammonium solution with regard to their suitability as solvents for cellulose for fluidity measurements. Cuprammonium solution dissolves low-fluidity celluloses more readily than does either Triton F or the xanthating mixture. Although any of the solutions could be used for evaluating cellulose, the latter have no advantage over cuprammonium as a standard solvent.

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I. INTRODUCTION

The fluidity of a solution of a cellulosic textile in some suitable solvent is a sensitive measure of the extent to which the cellulose has been degraded, for example, by bleaching agents, acids, alkalies, light, or mildew. Cuprammonium has been used extensively [1][2] as the solvent, but considerable care and special equipment are required for its preparation, storage, and use [2]. Accordingly, the possibility of using other solvents was investigated.

Certain quaternary ammonium bases swell cellulose and in some instances dissolve it. Dimethyldibenzylammonium hydroxide, hereafter called Triton F, the name used by the manufacturer,[3] is a good solvent for cellulose [3, 4, 5]. Sodium hydroxide-carbon disulfide mixtures convert cellulose to cellulose xanthate, and the fluidities of the xanthate solutions are related [6] to the quality of the cellulose.

The xanthate mixture has been used in some commercial laboratories for evaluating celluloses of special kinds, such as wood pulps. The present study is concerned with conditions under which celluloses of widely different degrees of degradation can be evaluated with the

[1] Research Associate at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate the literature references at the end of this paper.
[3] The Triton F used in the experiments was obtained through the courtesy of Röhm & Haas Co., 222 West Washington Square, Philadelphia, Pa.

aid of the three solvents. The advantages and disadvantages of each solvent are discussed.

II. PREPARATION OF CELLULOSES OF DIFFERENT DEGREES OF DEGRADATION

Cotton cellulose in the form of unbleached muslin cloth was used for this work. The muslin was first desized by steeping it overnight in a solution of a starch- and protein-solubilizing enzyme. It was then agitated for 2 hours in a boiling 1-percent solution of sodium hydroxide, rinsed with distilled water, then with 1-percent acetic acid, and again with water. The muslin was then dried and lightly pressed with a warm iron and cut from selvage to selvage into strips 7 inches wide.

Specimens were degraded to various extents by steeping them in hydrochloric acid and by overbleaching with calcium hypochlorite, and the effect of these treatments upon the breaking strength of the cloth was determined. The results of the fluidity tests can thus be related to data having direct practical value.

To prepare celluloses modified by acid, strips of the desized, alkali-boiled muslin were kept for 24 hours at 21° C in 1.01, 1.95, 2.92, 3.94, 4.90, and 5.98 *N* hydrochloric acid. The samples were removed, rinsed with distilled water, then with 0.5-percent ammonium hydroxide solution, extracted for about 16 hours with distilled water, and dried.

The chlorine solution for bleaching was prepared by making a paste with calcium hypochlorite and water. It was clarified by settling, and the supernatant liquid was drawn off and adjusted to contain approximately 1 percent of available chlorine. Strips of the desized muslin were steeped in the solution for ½, 1, 4, 9, 16, and 30 hours at 21° C. After the steeping, the muslin was rinsed with a 1-percent solution of sodium dithionite ($Na_2S_2O_4$),[4] rinsed with distilled water, and dried.

Specimens for the measurements of breaking strength were prepared by cutting the 7-inch strip of muslin into strips 6 inches long and 1¼ inches wide, with the warp yarns running lengthwise. Warp yarns were raveled from the edges until the strips were about 1 inch in width, each having 51 warp yarns. The strips were conditioned at 65-percent relative humidity at 70° F, and tests of breaking strength were made by the raveled-strip method [8] on a pendulum-type testing machine. The results are given in figures 1 and 2.

III. FLUIDITY MEASUREMENTS

The broken strips of muslin were used for the fluidity measurements. They were chopped in a laboratory Wiley mill to prepare well-mixed samples. This also facilitated attack by the solvents, although it did not degrade the cellulose.

All the solutions were prepared to contain 0.5 g of dry cellulose in 100 ml of solution.

The methods used for the preparation of cuprammonium solutions of cellulose and the measurement of their fluidities were the same as those previously described [2].

[4] Nomenclature recommended by the Committee of the International Union of Chemistry for the Reform of Inorganic Chemical Nomenclature, 1940 [7].

To dissolve cellulose in Triton F and in sodium hydroxide solutions containing carbon disulfide, the cellulose and reagents were placed in a mixing vial with glass plunger, described elsewhere [9], and rotated for 16 to 18 hours at 45° to 50° C.

In preparing viscose solutions for fluidity measurements, the required amount of cellulose was placed in the mixing vial and the air

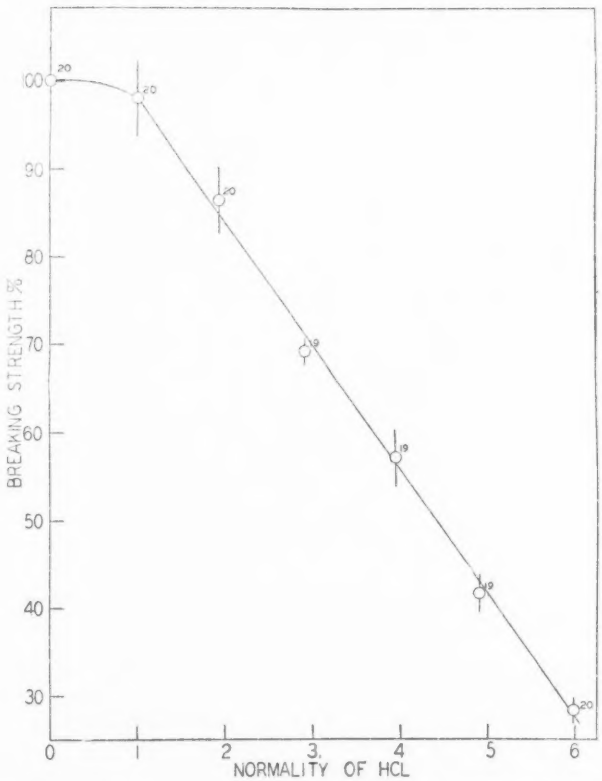

FIGURE 1.—*Changes in strength of the cotton fabric on treatment at 21° C for 24 hours with hydrochloric acid of different concentrations.*

The marked portions on the ordinates passing through the points represent the standard deviations for the respective values. The adjacent numerals are the number of observations, whose means are the points plotted.

in the vial swept out with a gentle stream of nitrogen. An amount of 16-percent sodium hydroxide solution, equal to ¼ of the volume (exclusive of plunger) of the vial, was added. The cellulose was permitted to soak for one quarter to one half hour, and afterwards an amount of carbon disulfide equal to five times the weight of the cellulose was added. The vial was then filled with a 7-percent solution of sodium hydroxide and rotated for 45 to 50 hours at a temperature of 15 to 18° C.

Pipette viscometers commonly used for measuring the fluidity of cuprammonium solutions of cellulose [2] were used, without modification, for measuring the fluidity of the viscose solutions. For the

Triton F solutions, which were more viscous, the same type of viscometer was used, except that the capillary discharge tube was larger, about 1.56 mm in diameter. All the viscometers were calibrated by the graphical method of Higgins [10, 11]. Those for the Triton F solution were calibrated with three oils of fluidities of approximately 0.52, 3.1, and 5.8 rhes.

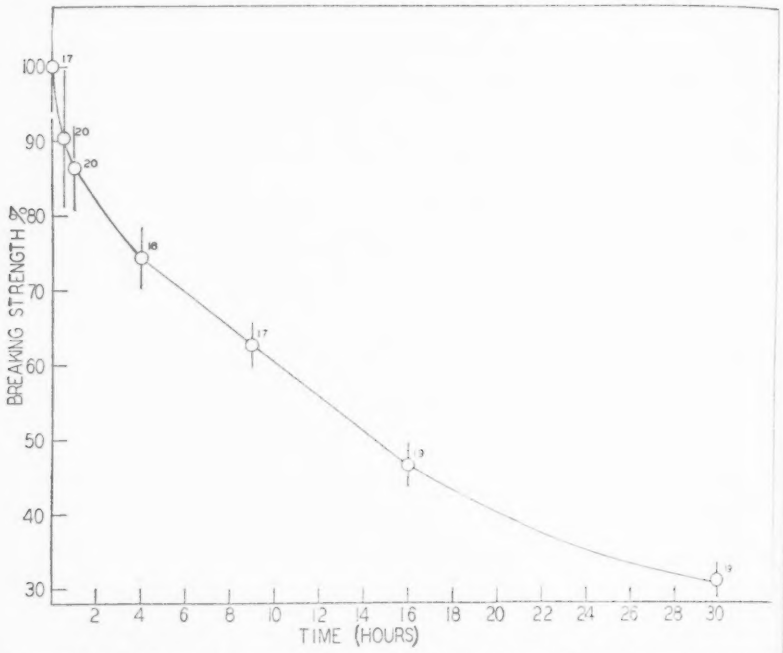

FIGURE 2.—*Decrease in strength of the cotton fabric steeped for different periods of time at 21° C in chlorine solution containing 1 percent of available chlorine.*

The data are plotted in the same manner described under figure 1.

The viscose and Triton solutions were brought to a temperature of 21° C and poured into the viscometer also at 21°. The flow measurements were made in the usual manner.

IV. RESULTS AND DISCUSSION

The results of the fluidity measurements are given in figure 3. For comparison, the Triton fluidity values were multiplied by 10 to make them nearly equal to the cuprammonium fluidities. This is the ratio found by other investigators [3]. It is apparent that any of the three solvents can be used.

The reproducibility of the results obtained was approximately equal for the three solutions in evaluating cellulose treated with hydrochloric acid. Therefore, the slopes of the curves in figure 3 may be taken as a measure of the relative sensitivity of the test. With the bleached muslin, however, the uncertainty of the measurements with the Triton F solution was about four times as great as that with the cuprammonium.

Although it may be concluded that the results obtained with either Triton F or mixtures of carbon disulfide and sodium hydroxide could be used instead of those obtained with cuprammonium solution for evaluating cellulose for some purposes, a comparison of the techniques required by each is desirable.

A concentration of Triton F of 1.96 *N* has been shown to be the best for dissolving cellulose [3, 4] and was used in these experiments. Although the Triton F rapidly swells cellulose, celluloses having a fluidity of 5 rhes or less in a 0.5-percent solution in cuprammonium

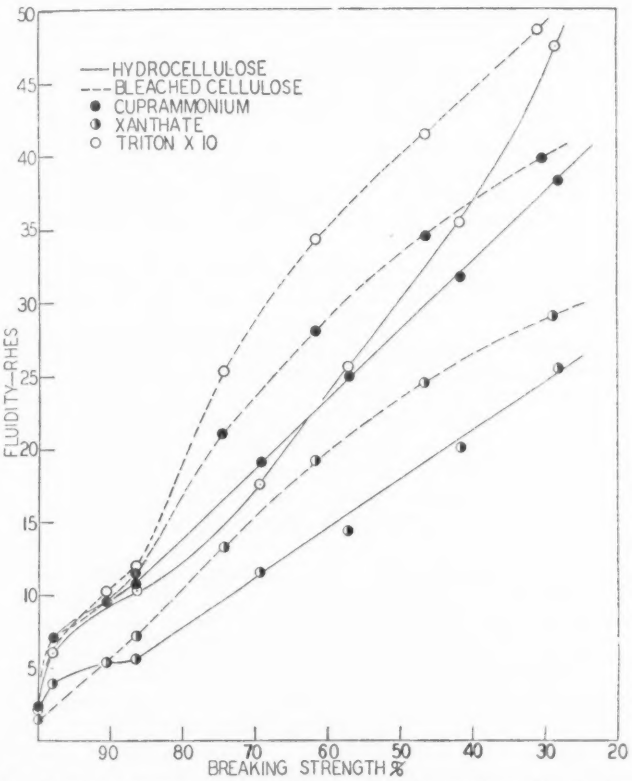

FIGURE 3.—*Breaking strengths and fluidities of acid-treated muslin (hydrocellulose) and of chlorine-treated muslin.*

require at least several hours to become homogeneously dispersed in Triton F at room temperatures. This was found to be true whether the mechanical agitation was applied by stirring, by shaking, or by a plunger in a closed container in the manner ordinarily used for dissolving cellulose in cuprammonium. Solutions of high-grade celluloses in the Triton are often clear in appearance but show swollen masses when the mixture is poured slowly from one vessel into another. The use of a water bath at 45 to 50° C while dissolving the cellulose increases the effectiveness of the agitation and facilitates dispersion. When agitated for 15 to 20 hours at this temperature, all the celluloses usually formed solutions suitable for measurements of fluidity.

Less time is required for preparing solutions of cellulose in cuprammonium. It is usually convenient, however, to permit the agitation to proceed overnight. Thus the time to be allotted for dissolving cellulose in either Triton or cuprammonium solution may be considered the same.

When this work was undertaken, Triton F was not readily available. Accordingly, it was recovered by the method described by Russell and Woodberry [3] and was used repeatedly. The recovery requires the addition of a considerable volume of reagents, and the concentration of the diluted Triton by the removal of water by distillation at reduced pressure. This seems to require at least as much time and work as the preparation of the cuprammonium solution. In addition, it was observed that Triton F which had been recovered several times, although adjusted to 1.96 *N*, was considerably more viscous than when first used. It is probably necessary, therefore, to control the conditions of recovery more closely and to specify properties other than normality in order to insure reproducible results with different lots of Triton. The possible variation of different lots of Triton F, although of the same titratable base, has been previously noted [3, 5].

The mixture of carbon disulfide and sodium hydroxide also has disadvantages which should be carefully considered when choosing a standard solution for the evaluation of celluloses. Some of these are the difficulty of dissolving celluloses which form solutions of low fluidity characteristics and the spontaneous coagulation of the cellulose solutions. Solution can be facilitated by the use of mixtures relatively high in carbon disulfide. The amount which may be added, however, is limited, since droplets of carbon disulfide in the solution introduce errors in the fluidity measurements and the larger amounts of carbon disulfide hasten the spontaneous coagulation. The rate of coagulation also depends upon the degree of degradation of the cellulose.

As a result of experiments with mixtures of different proportions of carbon disulfide and sodium hydroxide, the xanthating mixture described in section III was used. The results are given in figure 3. By agitating for 50 hours, the mixture produced, for all specimens of cellulose, solutions that could be used for fluidity measurements. That 50 hours was about the minimum time to be allowed for agitation was indicated by close visual examination of the solutions, which showed them to be nonhomogeneous. They contained what appeared to be swollen particles of cellulose. The particles were so small, however, that they did not interrupt the flow through the capillary of the viscometer. Although coagulation of the cellulose from these solutions took place after considerable time, changes in the solutions occurred very slowly. Fluidity measurements of fair reproducibility could be made within a few hours after agitation for 50 to 75 hours.

V. SUMMARY

Chemical degradation in cotton fabrics, exhibited by changes in breaking strength, can also be evaluated by fluidity measurements on solutions of the cotton in Triton F, sodium hydroxide-carbon disulfide mixture, or cuprammonium solution.

The sensitivity of the measurements in detecting changes in cellulose was found to be approximately the same for the three solutions

when evaluating cellulose degraded by acid. The sensitivity was least for the Triton when used on chlorine-bleached cotton.

Both Triton F and sodium hydroxide-carbon disulfide mixtures were found to require longer times to disperse unmodified cotton cellulose in a state satisfactory for fluidity measurements than is required by cuprammonium solution.

A comparison of the technique, time required, precision and sensitivity of the results obtained showed no advantage in substituting either Triton F or sodium hydroxide-carbon disulfide mixture as standard solvents in place of cuprammonium for evaluating celluloses of widely different states of degradation.

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[3] Ind. Eng. Chem., Anal. Ed. **12,** 151 (1940).
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[10] Nat. Phys. Lab. Collected Researches **11,** pt. 2, Viscometry 3 (1914).
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WASHINGTON, September 12, 1941.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1442

Part of Journal of Research of the National Bureau of Standards, Volume 27
December 1941

AN IMPROVEMENT IN THE METHOD FOR DISSOLVING CELLULOSE IN CUPRAMMONIUM SOLUTION FOR FLUIDITY MEASUREMENTS

By Ralph T. Mease

ABSTRACT

The use of mixing vials in place of the usual calibrated viscometers as vessels for dissolving cellulose in cuprammonium solution is described. The solution of cellulose is prepared in the vial and poured into a calibrated viscometer for flow measurements. The data given show that the exposure of the solution to the air for the short time required for pouring has no measurable effect on the fluidity.

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I. INTRODUCTION

In determinations of the fluidity of cuprammonium solutions of cellulose, the solution is usually prepared [1] [2] in the viscometer. A steel plunger is placed in the mixture of cellulose and cuprammonium solution and the viscometer rotated end over end. During this operation it occasionally happens that when celluloses, which swell and mix slowly with the liquid, are to be dissolved, the plunger drags cellulose to the ends of the viscometer and plugs the capillary. Also, the notched end of the plunger repeatedly strikes the narrowed end of the viscometer and may break it.

Cuprammonium solutions when in contact with air may be changed because of loss of ammonia and absorption of oxygen [3]. It was largely because of this instability that the solution of cellulose was prepared in the viscometer. It has been found, however, that the solutions of cellulose can be prepared in another vessel and transferred to the viscometer without measurable change in fluidity.

This paper describes an improved technique for dissolving cellulose, in the absence of air or any gas, in mixing vials. The technique permits the reservation of viscometers as instruments for flow measurements only. It is the result of experiments to prepare solutions of cellulose in dimethyldibenzylammonium hydroxide, and as the

[1] ASTM Designation D-539-39T. ASTM Standards, pt. 3, p. 981 (1939).
[2] J. Research NBS **22**, 271 (1939) RP1179.
[3] Ind. Eng. Chem., Anal. Ed. **13**, 322 (May 15, 1941).

xanthate, for fluidity measurements.[4] Data on fluidity measurements obtained with the usual method for effecting dispersion of cellulose in cuprammonium and with this method are presented.

II. PREPARATION OF THE CELLULOSE SOLUTION

Equipment suitable for dispersing celluloses in cuprammonium solutions is illustrated in figure 1. It consists of a mixing vial, *V*, fitted with a glass or iron stopper, *S*, and a glass plunger, *P*. It is desirable that the vial and plunger be so shaped that swollen cellulose will not adhere long to any part of the vial as it is rotated to effect solution.

To prepare a solution of cellulose for fluidity measurements, the vial containing the plunger is half filled with cuprammonium solution, and the required amount of cellulose is added and wetted with the

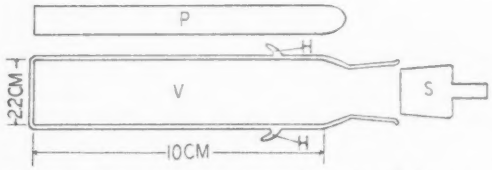

FIGURE 1.—*Mixing vial for effecting dispersion of cellulose in cuprammonium solution.*

V, Glass body of vial; *S*, glass or metal stopper; *P*, glass plunger. Flat end of plunger placed at bottom of vial when filling with cellulose and cuprammonium solution; *H*, hooks for rubber bands used to hold on stopper.

solution. More solution is then added until insertion of the stopper displaces all the air, with some of the cuprammonium solution overflowing. The stopper is held in place with rubber bands passing around the hooks, *H*, and the vial is attached to a wheel and rotated about its long axis at 50 to 55 rpm until solution is completed. It usually is convenient to rotate the vials overnight. While effecting solution, it is well to keep the temperature from rising above 25° C. This can be done by placing the equipment in a room held below this temperature or by mounting the wheel in a trough through which cool tap water is flowing. Measurements made on celluloses dissolved at 13° and 25° C showed that temperature changes within this range during the preparation of the solution had no appreciable effect on the fluidity. After solution is complete, the vial and contents are placed in a constant-temperature bath, and after reaching temperature equilibrium, the contents are poured into a calibrated viscometer at the same temperature and the flow measurements made in the usual manner. While transferring the liquid from the vial to the viscometer, the capillary end of the viscometer should be closed. This may be done by slipping a short piece of plugged rubber tubing over the capillary. The tubing is removed, and the usual observations are made on the moving meniscus as the liquid drains from the viscometer.

[4] J. Research NBS 27, 543 (1941) RP1441.

III. FLUIDITY MEASUREMENTS

The fluidity of the cellulose solution is not changed appreciably in the short time it is exposed to the air by the new technique. This is shown in table 1, which gives the results of measurements made at 21° C on 0.5-percent solutions of celluloses of different viscosity characteristics. The results in the left columns for the three samples were obtained by effecting solution in the viscometers with the metal plungers. The measurements were made with the viscometers used for preparing the solution. The second column gives the results of measurements on solutions prepared in the mixing vials and then transferred to a viscometer for measuring. The reproducibility of the results obtained by the two methods is approximately the same except for sample 3, for which it is somewhat better for solutions prepared in the mixing vials. More consistent results may be expected when using the vials, because of the more thorough mixing.

TABLE 1.—*Fluidity, in rhes, of celluloses of different flow characteristics*

Sample number—					
1		2		3	
Viscometers [a]	Vials [b]	Viscometers [a]	Vials [b]	Viscometers [a]	Vials [b]
2.67	2.72	12.0	12.0	17.9	17.4
2.53	2.74	12.0	12.0	17.5	17.5
2.66	2.71	11.9	12.0	18.0	17.3
2.69	2.62	11.9	11.9	17.3	17.4
2.61	2.61	11.7	11.9	17.6	17.4
2.65	2.68	11.9	12.0	17.7	17.5
2.68	2.61	11.9	12.6	17.4	17.5
2.68			12.3	17.4	17.4
Mean.. 2.65	2.67	11.9	12.1	17.6	17.4

[a] Cellulose solutions prepared in viscometers.
[b] Cellulose solutions prepared in mixing vials and transferred to viscometers for measurement.

WASHINGTON, September 30, 1941.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1443

Part of Journal of Research of the National Bureau of Standards, Volume 27, December 1941

A RESISTOR FURNACE, WITH SOME PRELIMINARY RESULTS UP TO 2,000° C

By R. F. Geller

ABSTRACT

A laboratory furnace, electrically heated with special oxide resistors, is described. The atmosphere within the furnace is oxidizing, and definite heating and cooling schedules can be maintained. Results are given of preliminary tests in which ThO_2, ZrO_2, BeO, CeO_2, MgO, and Al_2O_3 were heated singly or in various combinations in the temperature range from 1,800° to 2,000° C.

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I. INTRODUCTION

The attaining of temperatures above about 1,800° C, under conditions which can be controlled satisfactorily for the maturing of preformed shapes as practiced in the ceramic art, involves, generally speaking, a reducing atmosphere. This is true of the furnace developed by Arsem [1],[1] who used a graphite resistor, and of the high-frequency induction furnace [2] when graphite is used as the heating element. The electric arc also is available for high-temperature work, and reducing conditions can be avoided [3]. However, neither the electric arc, nor a source of heat such as the oxyhydrogen and oxyacetylene flames, has been adapted to the heating of preformed articles.

Research laboratories have long needed equipment in which investigations, such as phase-equilibria studies, could be carried above the 1,600° C, which is the approximate upper limit of platinum-rhodium wire-wound furnaces. Increasingly higher temperatures, at present approaching 1,800° C, are being used in the manufacture of special ceramics, and it is to be expected that furnaces producing from 1,800° to 2,000° C will soon find industrial application. Tungsten and molybdenum wire-wound furnaces [4] have been used in the

[1] Figures in brackets indicate the literature references at the end of this paper.

laboratory; but here again the furnace atmosphere must be free from oxygen, and the cost of the wire would make such an installation impracticable for industrial purposes.

It was to meet the need for a furnace in which specimens could be heated on a definite schedule, and in an oxidizing atmosphere, that the heating units described in this paper were developed. In this work the development of a unit based on principles which could be applied to industrial heating was kept in mind.

The idea of using electrically heated oxide resistors of the Nernst filament type is not new. Nernst [5] himself experimented with such resistors, but dropped the idea in favor of an iridium resistor for his laboratory. Also, small furnaces [6] heated with oxide resistors were used to "bake" the filaments then being made for the Nernst lamp.

In Harker's furnace [6] the resistor, in the form of a tube from 9 to 10 mm in diameter and 60 to 100 mm long, formed the wall of the heating chamber. It appears that difficulty was experienced in maintaining satisfactory contact between the resistor and the platinum lead-in wires, and also in obtaining a resistor sufficiently uniform and free from cracks to conduct the current satisfactorily. The cracks are caused by the large decrease in volume which takes place when the resistors become conducting for the first time and are heated to a temperature well above that at which they are heated preparatory to use. These and other shortcomings of the earlier furnaces were considered in the design of the furnace described in this paper.

II. FURNACE DESIGN AND CONTROL

Many compositions and designs of heating units were experimented with, the object being to (a) obtain a resistor of sufficiently low electrical resistivity to become conducting, with the available maximum potential of about 700 volts, at an easily obtainable temperature; (b) have enough temperature drop from the resistor to the lead-in wires so that the metal would not melt; and (c) maintain good contact with the metal.

There was sufficient information in the literature [7] to permit the selection of promising compositions for experimentation. For the resistor of the type shown in figure 1, tests showed a mixture containing 85 percent of electrically fused ThO_2 and 15 percent of CeO_2 (composition 4, table 1 and fig. 2) to be satisfactory, but the use of Y_2O_3 (compositions 21 and 22) instead of CeO_2 reduced the resistivity materially (table 1). Also, the ThO_2-Y_2O_3 resistors became conducting at a much lower temperature, as shown by the curves in figure 2. Resistors having even a relatively low ZrO_2 content, such as composition 12 (table 1), deformed when the furnace was heated above 1,800° to 1,850° C. For the contact blocks, it is desirable to have a composition of appreciably higher electrical conductivity than that of the resistor, and for this purpose a mixture containing 85 percent of ZrO_2 and 15 percent of Y_2O_3 was used. As figure 1 shows, the metal conductors, composed of 60 platinum–40 rhodium wire, were cast into the contact block so that the block would shrink against the metal and maintain contact.

The design of the furnace used for the preliminary tests is shown in figure 3. The choice of materials was governed by their melting points, by the eutectic temperature of any two materials in mutual contact, and by their electrical conductivity at high temperatures.

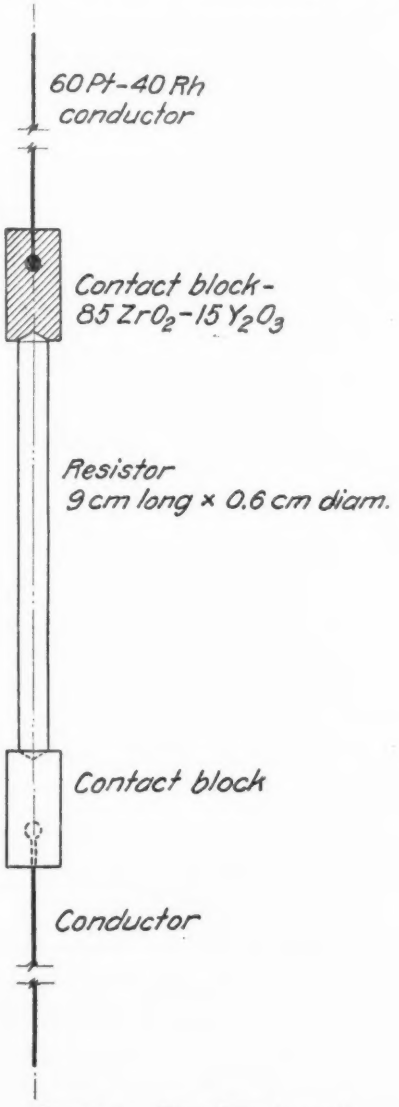

FIGURE 1.— *Typical heating unit.*

For example, ZrO_2 is not used for the innermost parts because its conductivity might cause short circuits [8]. On the other hand, the ZrO_2 is suitable for separating the ThO_2 and Al_2O_3, this separation being necessary because ThO_2 and Al_2O_3 react at about 1,900° C to form a liquid of rather low viscosity.

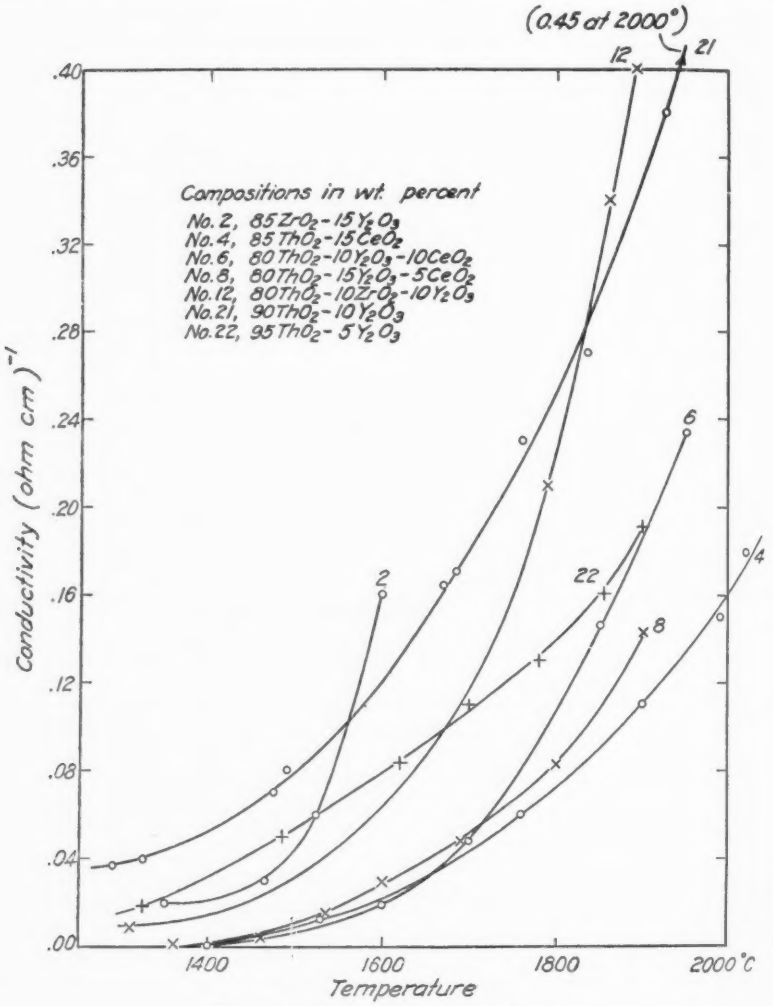

FIGURE 2.—*Conductivity of resistors.*

These conductivity values are purely relative. They are calculated from the current, the over-all resistance of a heating unit, and the temperature of the specimen rather than of the resistor itself.

TABLE 1.—*Electrical conductivity of resistors (ohm cm)*$^{-1}$

[Values are taken from the curves in figure 2 and are purely relative]

Resistors		Conductivity at (°C)—							
No.	Composition (wt percent)	1,300°	1,400°	1,500°	1,600°	1,700°	1,800°	1,900°	2,000°
		Mho	*Mho*	*Mho*	*Mho*	*Mho*	*Mho*	*Mho*	*Mho*
2	85 ZrO_2, 15 Y_2O_3	------	0.021	0.044	0.16	(a)	------	------	------
4	85 ThO_2, 15 CeO_2	------	.001	.010	.024	0.043	0.074	0.11	0.16
6	80 ThO_2, 10 Y_2O_3, 10 CeO_2	------	.001	.006	.020	.050	.10	.19	------
8	80 ThO_2, 15 Y_2O_3, 5 CeO_2	------	.003	.010	.030	.050	.085	.14	------
12	80 ThO_2, 10 ZrO_2, 10 Y_2O_3	0.010	.014	.030	.064	.11	.23	.41	------
21	90 ThO_2, 10 Y_2O_3	.038	.050	.076	.12	.18	.25	.35	.45
22	95 ThO_2, 5 Y_2O_3	.015	.030	.042	.078	.11	.14	.19	------

[a] Deforms.

The available data on the materials used for the resistors, and for the innermost parts of the furnace, are given in section III–2.

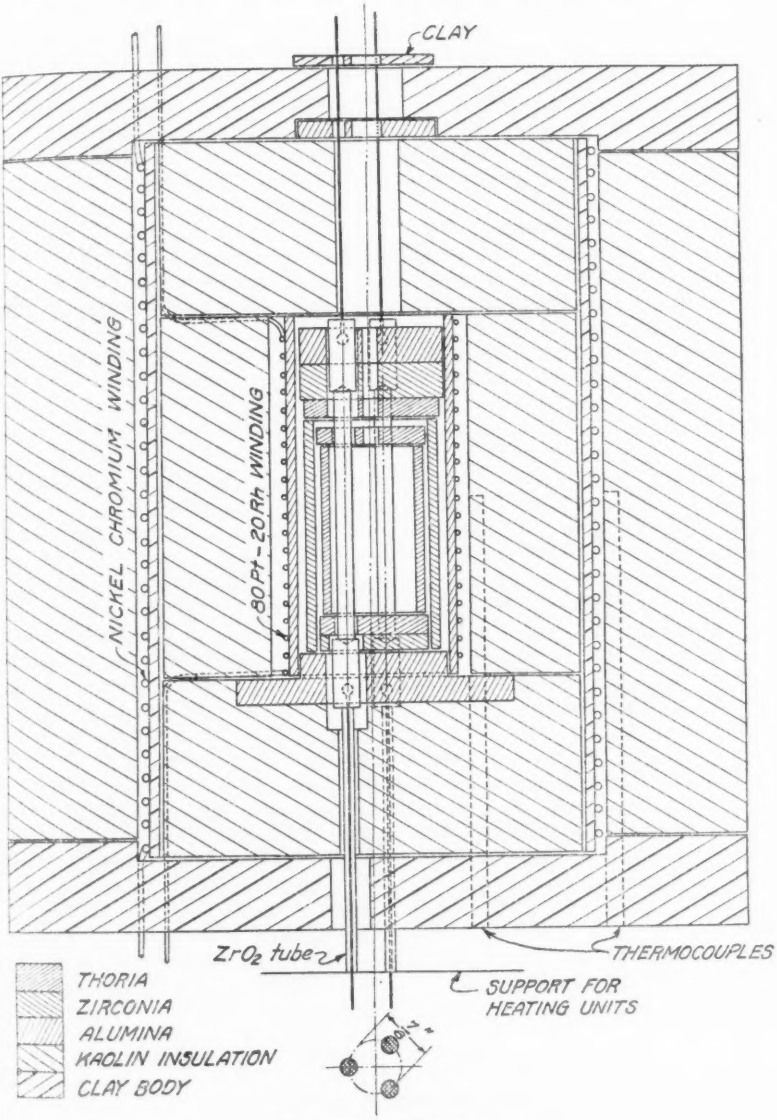

FIGURE 3.—*Furnace.*

In this furnace, the 80 platinum-20 rhodium coil is wound on an Alundum core 5 in. long and 2¼ in. ID. The three resistors are equally spaced on a circle of ⅞-in. diameter. Other dimensions may be scaled from the drawing.

For the furnace shown in figure 3, the 80 platinum–20 rhodium heating coil is wound on a 2½-in. ID Alundum core, and three resistors[2]

[2] In discussing the furnace, the metallic heating elements will be referred to as "coils," and the oxide resistors simply as "resistors."

are equally spaced on a circle of ⅞-in. diameter. The thermocouples placed next to the platinum-rhodium (Pt-Rh) and nickel-chromium (Ni-Cr) coils are needed to guard against overheating of the coils. A larger furnace has been built in which the Alundum core is 4 in. ID and eight resistors are equally spaced on a circle of 2¼-in. diameter. For still larger units, it would be feasible to eliminate the Pt-Rh coil and heat the furnace to the conducting temperature of the resistors with gas flames, or with removable resistors of the Globar type.

Transformers of the Variac type, operating on 110-volt lines, are used to control the current through the Ni-Cr and the Pt-Rh coils. This current was gradually decreased as more and more heat was dissipated from the resistors. The current through the Pt-Rh coil was usually discontinued after the specimen temperature exceeded about 1,900° C. The current through the resistors is controlled with a step-up transformer, delivering 220 or 440 volts, connected in series with a Variac transformer delivering from 0 to 270 volts. The Variac can be used alone, or the voltage may be additive to the voltage from the step-up transformer. In this way, the potential drop across the resistors may be varied continously from 0 to about 700 volts. Close voltage control is essential, since the current through the resistors (3 to 8 amperes) must be held within ±0.05 ampere to hold the temperature within ±5° C in the small furnace (fig. 3). In addition, rheostats and tungsten filament lamps are connected in series with each resistor. The rheostats are used to balance any inequalities in the resistances of the heating units, while the lamps act as ballast resistances and greatly increase the stability of the heating current.

With about 6 amperes at 80 volts passing through the Ni-Cr coil and no current through the Pt-Rh coil, the specimen temperature can be held at 2,000° C with a total of about 7 amperes, and a voltage drop of 130, through the three resistors. These values are typical for 90 ThO_2-10Y_2O_3 resistors averaging 9 cm long and 0.6 cm in diameter.

The accuracy of the temperature measurements, made with an optical pyrometer, was checked by reading the temperature at which samples of a platinum wire (melting point [9] 1,773° C), a furnace winding of nominally 80 platinum–20 rhodium composition (melting point [10] approximately 1,900° C), and a wire of nominally 60 platinum–40 rhodium composition (melting point [10] approximately 1,945° C) were observed to melt. In the first case the reading obtained was 1,777° C, in the second case it was 1,890° C, and in the third case it was 1,935° C. Since the optical pyrometer calibration was certified to ±10° C, the above observations indicate that the over-all inaccuracies of the temperature measurements were within the limits of certification of the instrument.

III. RESULTS

1. HEATING ELEMENTS

The conductivity values plotted in figure 2 and given in table 1 are relative and approximate only. They are calculated from the current and from the potential drop across the heating unit, including the resistor proper and the contact blocks. Also, the temperatures given in table 1 and plotted in figure 2 are those obtained by sighting the optical pyrometer on the specimen and therefore do not represent the temperatures of the resistors themselves. These temperatures

were, of necessity, higher. The observed conductance of a heating unit was invariably lower while heating than while cooling the furnace, showing that better contact had been established at the highest temperatures. The conductance was also lower for "new" resistors. For example, the current through new resistors of composition 21 (table 1) increased slowly at 1,450° C under 540 volts. After the resistors had been used previously in heating the furnace, the current started to flow through them at 960° C, and built up rapidly, at 540 volts, or at 1,050° C at 350 volts.

The data plotted in figure 2 were obtained with previously used resistors and during the cooling of the furnace.

2. MATERIALS AND EXPERIMENTAL MIXTURES

The materials described in this section were used in the construction of the furnace, and in the resistor units and experimental

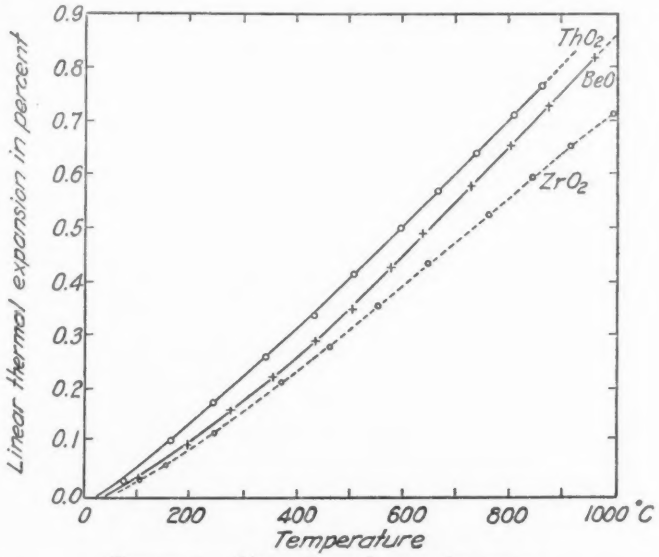

FIGURE 4.—*Linear thermal-expansion curves.*

These curves were obtained on specimens which had been heated at 2,000° C for 10 minutes. The determinations were made by A. S. Creamer.

mixtures. Most of the specimens were heated to determine the possibilities of the various oxide combinations for high-temperature work, and a few mixtures were tested as preliminary steps to future phase-equilibria studies.

Thoria.—This material was described by the producer as containing at least 99 percent of ThO_2. It was used in preparing the resistors and furnace parts. A specimen, heated to 2,000° C, was nonporous, hard, and brittle. The linear thermal expansion is shown in figure 4, and the X-ray pattern was that of a face-centered cubic structure with $a=5.57$A.

Zirconia.—Material described by the producer as containing over 97 percent of ZrO_2 was used for the furnace parts, and material of over 99-percent purity was used for the contact blocks, experimental resistors, and body mixtures. Both had been electrically fused. The

X-ray pattern of a sample of ZrO_2 heated to 2,000° C was too complex to analyze; its linear thermal expansion is shown in figure 4.

Yttria.—At best, this material should be considered as predominantly Y_2O_3. A spectrogram showed medium to strong lines for Dy, La, Nd, Sm, Sr, and Yb.

Ceria.—This oxide was obtained from several sources, but none of the samples was analyzed. An especially purified sample, prepared by C. J. Rodden, was heated at 2,005° C for 5 minutes in an iridium container. After this treatment, the color was a pale buff and it was found to have sintered. This behavior shows that the melting point is above 2,000° C, as shown by Wartenburg and Gurr [11], and that the value 1,950° C, given by Ruff [12], is low.

Beryllia.—This was commercial material, described by the producer as of high purity, containing approximately 0.003 percent of Fe and 0.004 percent of CaO. The X-ray pattern of a specimen heated to 1,900° C contained the lines for crystalline BeO, as given by Wykoff [13]. The linear thermal expansion of a sample heated to 2,000° C is shown in figure 4. There was no fusion between this sample and the ThO_2 base on which it was heated.

Magnesia.—This was commercial electrically fused material. It was semitransparent and with a blue-green tint in the massive form. Heating to 1,980° changed the tint to yellow. Petrographic examination showed over 90 percent of periclase. The diffraction pattern showed the lines for periclase plus some additional lines which were not identified.

Alumina.—Some of the alumina had been especially purified from the nitrate by E. N. Bunting and contained about 99.95 percent of Al_2O_3. The rest was commercial fused Al_2O_3 of about 99.8 percent purity.

Thoria and zirconia.—A specimen of ZrO_2, when heated on a ThO_2 base to 2,000° C, showed no evidence of reaction at the contact. An intimately mixed sample of the two oxides, in 1:1 mole ratio, heated at 2,010° C for 10 minutes, and again at 2,000° C for 10 minutes, showed a very dense, hard, structure after each heat treatment, and the X-ray patterns showed the lines for ThO_2 and for ZrO_2. The presence of each phase was further verified by petrographic examination. The linear thermal expansion, however, (fig. 5) corresponded to the expansion reported by Merritt [14] as being that of the compound $ThO_2.ZrO_2$. The linear expansion of a specimen of the material originally reported on by Merritt was redetermined (fig. 5). Reexamination of this specimen by H. Insley showed the presence of ThO_2 and of ZrO_2 identically as found in the sample prepared in this study The X-ray patterns do show that the unit cell of ThO_2 had been decreased so that $a=5.53$ A, indicating that the ThO_2 had taken some ZrO_2 in solid solution. The conclusion must be drawn that ThO_2 and ZrO_2 did not react to form a compound. This is in accord with the findings of Ruff, Ebert, and Woitinek [15].

Thoria and alumina.—Al_2O_3 of 99.95 percent purity, when heated at 1,850° C for 10 minutes in a ThO_2 crucible, was unaffected. When heated at 1,900° C for 10 minutes, there was partial fusion. When heated at 1,950° C, a very fluid melt was formed. These data support the finding of Wartenburg and Reusch [16] of a eutectic melting at about 1,900° C.

Thoria and magnesia.—An intimate mixture in the mole ratio 40

ThO_2 to 60 MgO, heated in a magnesia crucible at 2,010° C for 10 minutes, showed sintering but no evidence of fusion. This indicates that the eutectic is above 2,000° C. The X-ray pattern contained the lines for periclase (MgO) and for crystalline thoria, with no change or shift from lines for either material heated alone. In the above experiment there was no reaction between the MgO crucible and the ThO_2 base upon which it was placed.

Zirconia and alumina.—After heating at 1,955° for 5 minutes, Al_2O_3 in a ZrO_2 crucible had not reacted with the crucible. After

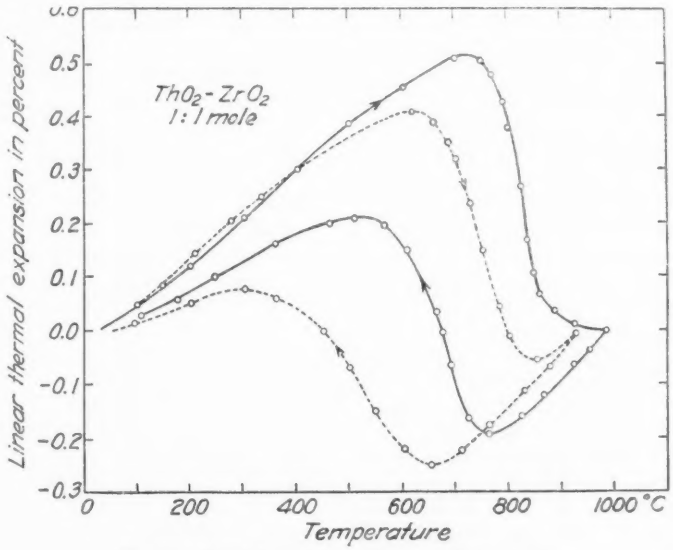

FIGURE 5.—*Linear thermal-expansion curves.*

The values connected with the continuous line were obtained on a specimen made of ZrO_2 and ThO_2 in 1:1 mole proportions and twice heated to approximately 2,000° C for 10 minutes. The values connected with the broken line were obtained on a sample originally reported on by Geo. E. Merritt (Trans. Am. Electrochem. Soc. **50**, 165, 1926) and made by fusion at about 3,500° ±500° C. (The determinations were made by A. S. Creamer.)

heating to 1,990°, it had reacted to form a vesicular mass. The X-ray pattern of this vesicular material gave only the lines for monoclinic ZrO_2 with a slightly decreased unit cell, indicating solid solution of Al_2O_3 in the ZrO_2. When, however, an intimate mixture, in equal mole ratio, of ZrO_2 and Al_2O_3 (99.9-percent purity) was heated in a ZrO_2 crucible at 1,940° C for 15 minutes, a friable, highly vesicular mass was produced. The diffraction pattern showed strong lines for ZrO_2, and weak lines for alpha-corundum, with no shift in the lines for either phase. A eutectic at 1,920° C is reported by Wartenburg, Linde, and Jung [17] for approximately 1:1 mole proportions of Al_2O_3 and ZrO_2.

Zirconia and beryllia.—There was marked attack on the ZrO_2 crucible when BeO was heated in it at 1,975° C for 15 minutes. The X-ray pattern showed the lines for BeO and for ZrO_2, with no change or shift from the lines for either phase. Wartenburg and Gurr [11] show a eutectic temperature at about 2,250° C with 35 mole percent of ZrO_2. There was no fusion when shapes were heated in contact at 1,925° C.

Beryllia and ceria.—A mixture of 21 BeO–79 CeO_2, in weight percent (1.83:1 mole ratio), heated at 1,985° C for 10 minutes showed incipient fusion. The diffraction pattern contained the lines for BeO, with no shift in position, and also lines which were not identified but were probably those of CeO_2. This agrees fairly well with Wartenburg and coworkers [18], who report the above mixture as a simple eutectic melting at about 1,960° C.

Magnesia and alumina.—A mixture of spinel composition was heated in a MgO crucible at 1,980° for 20 minutes. The mixture had sintered to a dense, hard, and coarsely crystalline mass which had not attacked the crucible. Petrographic examination showed about 85 percent of large isotropic plates of spinel with isotropic inclusions of higher index, probably periclase. The X-ray pattern gave lines for spinel ($MgO.Al_2O_3$) and for periclase, the lines for spinel being the stronger.

The diagram for the system MgO-Al_2O_3 [19] shows spinel as melting at 2,135° C, and eutectics containing 92 percent of Al_2O_3 at 1,925° C, and 55 percent of Al_2O_3 at 2,030° C.

Magnesia and beryllia.—A study of this system, and of the system alumina-beryllia, should be of particular interest to manufacturers of special insulators, such as those used in spark plugs.

Ruff and coworkers [20] reported the melting of equal parts, by weight (0.62:1 mole ratio), of MgO and BeO at about 1,960° C. Wartenburg [18] published a melting curve for this system which resembles that of Ruff, but the lowest melting point is at about 1,860° C. In an earlier report, Wartenburg and Prophet [21] had obtained the eutectic at about 1,670° C. Accordingly, mixtures in the same weight proportions (50–50), were heated for 15 minutes in magnesia crucibles at 1,800° C, at 1,845° C, and at 1,900° C. After the first heat treatment the mixture was sintered, after the second it was partly fused, and after the last it was well fused. These results, therefore, support the Wartenburg value of 1,860° C.

Beryllia and alumina.—The information published by Wartenburg [16] shows a fairly sharp eutectic at 1,890° C for a mixture of BeO and Al_2O_3 in the 1:1 mole ratio. He points out that there was no evidence of the formation of chrysoberyl.

Mixtures in the mole ratio 1 BeO:1 Al_2O_3 were heated in beryllia crucibles for 30 minutes at each of the following temperatures and with the results described:

1,800° C.—This sample was definitely porous. The X-ray pattern contained strong lines corresponding to those for chrysoberyl (BeO. Al_2O_3), and a weak line corresponding to the strongest line in the bromellite (BeO) pattern. The observed indices of refraction (1.732 minimum and 1.741 maximum) do not agree with those given for the mineral chrysoberyl (alpha=1.747, beta=1.748, gamma=1.757 [22]), but the lines for chrysoberyl in the X-ray patterns are identical with those for the mineral obtained from the National Museum, through the courtesy of E. P. Henderson, from a deposit at Topsham, Maine. The indices of refraction of this mineral sample were alpha=1.741, gamma=1.751. The patterns for the prepared samples contained also several lines which do not correspond to those for alpha or beta Al_2O_3, or for BeO.

1,825° C.—The specimen was vitrified and was practically one phase, with indices of refraction ranging from 1.732 minimum to 1.741

maximum. The crystals were platy. There was no free BeO or Al_2O_3 detectable with the microscope.

1,855° C.—This treatment produced uniform vitrification. The crystals were well developed, platy, and with indices ranging from 1.732 to 1.741. The X-ray pattern was identical with that for the sample heated at 1,800° C.

1,880° C.—The charge had fused to what must have been a liquid of low viscosity, since nearly all had been absorbed by the porous crucible. A few large, tabular crystals remained on the crucible bottom, and the diffraction pattern of chrysoberyl for these crystals was identical with the patterns for the samples heated at 1,800° C and at 1,855° C. The indices of refraction ranged between 1.732 and 1.741. The melting point of this chrysoberyl lies between 1,855° and 1,880° C. Weigel and Kaysser [23] report the melting point of sample of mineral chrysoberyl as 1,817° ±6° C.

All of the X-ray diffraction patterns described in this paper were prepared and interpreted by H. F. McMurdie. The powdered samples were mounted on fine glass rods in the center of cylindrical cameras, having radii of about 5.7 cm, and were rotated during exposure to the CuKα radiation.

IV. SUMMARY AND DISCUSSION

A furnace is described which is heated electrically with resistors of the Nernst filament type, supplemented with a Pt-Rh coil to bring the resistors to conducting temperature. The suitability of this furnace for laboratory tests involving oxidizing atmospheres, at temperatures above the upper limit of conventional "platinum-wound furnaces" (1,600° C), is considered to have been demonstrated. It is believed that heating units made on the same principles as those used in this work can be adapted also to larger furnaces, possibly in the commercial production of ceramic specialties. In larger furnaces, the heating coils could be replaced with gas flames, or with removable resistors of the Globar type.

The principal difficulty encountered in the operation of the furnace results from the "after-shrinkage" of the resistors, and of the ThO_2 and the ZrO_2 furnace parts. This shrinkage may cause deformation of the resistors, and almost invariably causes the progressive cracking of the furnace parts. It could probably be overcome by heating the shapes uniformly, prior to use, at a temperature appreciably higher than was possible in this work. The shapes and resistors used were cast, dried, and then given a preliminary heating at from 1,425° to 1,500° C.

Al_2O_3, BeO, CeO_2, MgO, ThO_2, and ZrO_2 were heated singly and in various combinations for periods of time ranging from 5 to 30 minutes, and at temperatures ranging from 1,800° to 2,000° C. The principal results, which are quite preliminary in nature, may be summarized as follows:

Shapes (a) of magnesia and of thoria, (b) of beryllia and of thoria, and (c) of zirconia and of thoria were heated in mutual contact at temperatures as high as 2,000° C without harmful effects.

No interaction occurred when (a) shapes of alumina and of thoria were heated in contact at 1,850° C, (b) shapes of alumina and of zirconia were heated under the same conditions at 1,900° C, (c) when shapes of beryllia and of zirconia were heated in contact at 1,925° C,

and (d) when shapes of magnesia and of beryllia, and of alumina and of beryllia, were heated in contact at 1,800° C and at 1,825° C, respectively. Considerable fusion did occur when the combinations in question were heated at temperatures approximately 50° C above those mentioned.

When an intimate mixture of zirconia and thoria in equimolecular ratio was heated at approximately 2,000° C, the product had an anomalous thermal expansion, showing a large reversal between approximately 500° and 1,000° C during both heating and cooling. This is in sharp contrast to the regular expansion of either thoria or zirconia after having been heated alone to 2,000° C, and cannot be explained by the formation of a compound since the X-ray patterns and petrographic examination show only the presence of the original oxides.

When an intimate mixture of magnesia and alumina in 1:1 mole ratio was heated at 1,980° C, the principal product was spinel.

When intimate mixtures of beryllia and alumina in 1:1 mole ratio were heated at from 1,800° to 1,880° C, the principal product, as shown by diffraction patterns, was chrysoberyl. This compound fused between 1,855° and 1,880° C.

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